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Trends
In Usage of
Antimony

A Report of the

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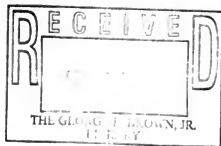
NATIONAL RESEARCH COUNCIL
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TRENDS IN USAGE
OF
ANTIMONY

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REPORT OF
THE PANEL ON ANTIMONY

of the
COMMITTEE ON THE TECHNICAL ASPECTS OF
CRITICAL AND STRATEGIC MATERIALS
NATIONAL MATERIALS ADVISORY BOARD
Division of Engineering - National Research Council



Publication NMAB-274

National Academy of Sciences - National Academy of Engineering
Washington, D. C.

December 1970

This report is one of a series in a study undertaken by the National Materials Advisory Board for the National Academy of Sciences and the National Academy of Engineering in partial execution of work under Contract No. GS-00-DS-(P)-94008 with the General Services Administration on behalf of the General Services Administration, the Office of Emergency Preparedness, and the Department of Commerce. Partial financial support of this contract was provided by the U.S. Bureau of Mines.

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CONTENTS

	<u>Page</u>
ABSTRACT	x
I. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS	1
II. INTRODUCTION	8
III. SUPPLY	9
A. World Resources	9
B. World Production	11
C. Domestic Supply	12
D. Production of By-Product Antimony	15
E. Imports	16
F. Smelter Production	16
G. Secondary Production	16
IV. CONSUMPTION AND PROJECTED DEMAND	19
A. Metallurgical Applications - Batteries	19
B. Metallurgical Additive in Products Other Than Batteries	33
1. Bearing Metals	33
2. Type Metal	33
3. Solder	33
4. Cable Covering	34
5. Ammunition	34
6. Miscellaneous	34
C. Chemical Uses - Flame Retarders	34
1. Impact of Legislation and Regulations	35
2. Consumption in Flame Retarders	38
a. Fabrics	40
b. Plastics	41
c. Rubber Products	43
d. Adhesives and Sealants	44
e. Paper	44
f. Summary of Flame Retarder Uses	44

CONTENTS (Continued)

	<u>Page</u>
D. Chemical Uses (Other than Flame Retarders)	45
1. Ceramics	45
2. Glass	47
3. Catalysts	48
a. Antimony Oxide	48
b. Antimony Chlorides	49
4. Stabilizers	49
5. Textile Dye Fixative	49
6. Ammunition, Matches, Fireworks, and Model Rocket Engines	50
7. Vulcanization of Rubber	50
8. Pigment	50
9. Textile Delusterants	50
10. Miscellaneous	51
11. Summary - Chemicals	51
E. Summary of Antimony Consumption and Demand to 1975	53
1. Consumption	53
2. Supply-Demand Balance	55
F. References	56
APPENDIX A - Stockpile Activities	59
APPENDIX B - Review of Technical Literature	65

TABLES

<u>No.</u>		<u>Page</u>
1	Primary Antimony Consumption in 1969 and Projected Demand to 1975, Tons Metal	4, 54
2	Summary - Chemical Use of Antimony	5, 52
3	World Production of Antimony	13
4	Antimony Mine Production and Shipments in U. S.	14
5	U. S. Imports of Antimony	17
6	Primary Antimony Processed in the U. S.	18
7	Secondary Antimony Recovered in the U. S.	20
8	By-Product Antimonial Lead Produced at Lead Refineries in the U. S.	21
9 } 10 } 11 }	Projected Antimony Consumption of Storage Batteries Through 1975	{ 26 { 27 { 28
12	Inventory of Government Stockpiled Antimony	62

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	U. S. Antimony Supply, Circa 1968, Short Tons Antimony	3
2	Antimonial Lead Consumption - Dollar Value	22
3	Tons Antimony Contained in Antimonial Lead - Dollar Value	23
4	Antimony Requirement for SLI and Equivalent Lead Acid Batteries - Projected to 1980	29
5	Antimony Requirement for Industrial Batteries Projected to 1980	30
6	Antimony Required for all Types Lead-Acid Batteries - SLI and Industrial Types - Projected to 1980	31

ABSTRACT

Over the 1969-1975 period, demand for primary antimony is expected to increase at an annual rate of 5.8 percent, or to a cumulative additional 25,000 tons of primary antimony, over 1969 production levels. Known world resources appear adequate to support present production for the above period. Sustained higher prices may stimulate increased production. Aside from its domestic resources, the U.S. antimony-consuming industry must look to its future sources of material from South Africa, Bolivia, and Australia.

As projected to 1975, the fastest growing areas of primary antimony demand are as flame retardants in plastics (12.4 percent annual growth) and as catalysts (11.6 percent annual growth). The annual growth rate (5.8 percent), projected to 1975, for total antimony demand is exceeded by the growth rates of all flame retardants (9.5 percent), colors (8.2 percent), and dye fixatives (7.0 percent).

Total metallurgical usage of antimony is expected to grow at 1.5 percent per year, a decreasing rate of demand. However, batteries are projected to continue at a 3.0 percent annual growth rate, a relatively steady demand.

The Panel recommended that consumption statistics should be revised to emphasize the functional usage of antimony. The method of reporting and tabulating consumption statistics to the Bureau of Mines should reconcile differences in flame retardants and uses in other product categories. The flame retardant section should indicate subsections for plastic, rubber, pigment, etc.

Another recommendation was that the U.S. Geological Survey and the Bureau of Mines conduct a resource evaluation based on antimony price levels such as \$0.50, \$1.00, \$1.50, and \$2.00 per pound.

1. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Reserves/Resources

The United States produces only about 5 percent of its primary antimony requirements from domestic sources. Most of the new primary production has been byproduct recovery associated with the smelting of lead and lead-silver ores. During periods of high demand and elevated prices in the past and as is the situation in early 1970, higher levels of domestic antimony output have been mined from deposits valued chiefly for their antimony content.

On a worldwide basis, known resources appear to be adequate to support present production, and sustained higher prices may stimulate increased production.

Recommendation: A need exists for more detailed knowledge of antimony resources, particularly in the United States and the Free World. It is recommended that an up-to-date resource evaluation be conducted by the Geological Survey and the Bureau of Mines and that the study be based on several price levels for antimony metal, such as \$0.50, \$1.00, \$1.50, and \$2.00 per pound antimony.

World Production

Plans for expansion of South Africa's antimony production capacity by approximately 50 percent were announced in 1969. The expansion to some 25,000 to 30,000 tons of annual output would increase South Africa's dominant role in the future world supply of antimony. Bolivia will likely remain the world's second largest supplier. Mexico, as well as the Sino-Soviet bloc countries, will probably maintain present levels of production but cannot be counted on to supply the growing needs of the antimony-consuming industry. Australia's output will increase substantially, but most of the expanded output is destined for Japanese smelters.

Domestic Supply

The U.S. antimony-consuming industry must look to three sources of material in the future: domestic, South African, and Bolivian. Sharp increases in domestic antimony production are anticipated, particularly from the Yellow Pine, Idaho, deposits. Production from the latter source could conceivably reach the 2,000 to 3,000 ton-per-year level in the next few years and thus provide some 10 to 15 percent of the domestic needs. Bolivia could expand production to satisfy a sizable portion of U.S. needs. The expanded output of South African sources, barring unfavorable political and marketing factors, could provide an increased portion of U.S. needs.

Demand

The Domestic Supply-Use Cycle in 1968 is illustrated in Figure 1. Domestic demand for primary antimony in 1975 is projected at 26,280 tons of metal. This represents an annual growth rate of 5.8 percent from a consumption level of 18,830 tons in 1969.

The fastest growing areas of primary antimony demand, as projected to 1975, are flame-retardant use in plastics (12.4 percent annual growth rate) and catalyst uses (11.6 percent annual growth). Total flame retardant growth (9.5 percent), colors (8.2 percent), and dye fixatives (7.0 percent) exceed the annual growth rate projected to 1975 for total antimony demand (5.8 percent). Consumption and demand data are summarized in Table 1.

All metallurgical uses, except batteries at a 3 percent annual growth rate, indicate steady or declining demand. Total metallurgical usage is expected to grow at a nominal 1.5 percent per year. The major tonnage increases of future growth in primary antimony demand will be in flame retardant applications. Chemical uses will maintain their share of future demand, while the relative demand for metallurgical applications will decrease. A summary of chemical uses with forecasts to 1975 appears in Table 2.

Supply Schema, Circa 1968

From information gathered by the Panel and complemented by Bureau of Mines data, a schema of antimony supply, circa 1968, was developed and is illustrated in Figure 1. Tonnage data have been rounded.

Figure 1. U.S. ANTIMONY SUPPLY, CIRCA 1968, Short Tons/Antimony

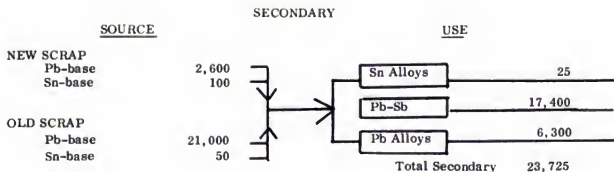
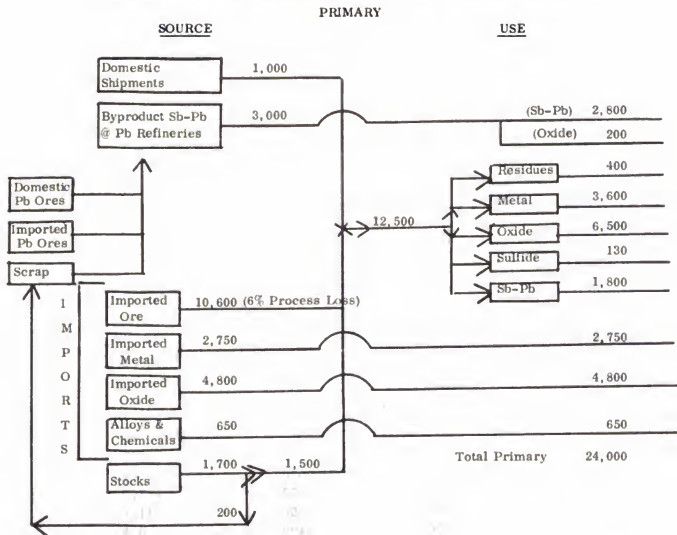


TABLE 1 Primary Antimony Consumption in 1969 and Projected Demand to 1975, Tons Metal

Use	1969 Estimated Consumption	1975 Projected Demand	Annual Growth Rate % 1969-1975
<u>Metallurgical</u>			
Batteries	5,950	7,080	3.0
Bearings	750	400	-11.0
Type Metal	400	400	0.0
Solder	225	225	0.0
Cable Covering	150	150	0.0
Ordinance	150	100	-7.0
Other	<u>225</u>	<u>225</u>	<u>0.0</u>
Subtotal	7,850	8,580	1.5
<u>Flame Retardants</u>			
Plastics	3,970	8,000	12.4
Adhesives	830	1,100	4.8
Rubber	460	620	5.1
Other	<u>1,420</u>	<u>1,780</u>	<u>3.8</u>
Subtotal	6,680	11,500	9.5
<u>Chemicals</u>			
Ceramics	1,850	2,500	5.1
Glass	780	650	-3.1
Catalysts	1,215	2,350	11.6
Colors	250	400	8.2
Dye Fixative	50	75	7.0
Pyrophorics	105	100	-0.8
Miscellany	<u>50</u>	<u>125</u>	<u>16.5</u>
Subtotal	<u>4,300</u>	<u>6,200</u>	6.3
Grand Total	<u>18,830</u>	<u>26,280</u>	5.8

TABLE 2. Summary - Chemical Use of Antimony

End Use	Chemical Formula	1969 Usage, Lbs		1975 Forecast* Lbs, Sb	Possible Replacement	
		Compound	Sb			
Ceramics	Sb_2O_3	3,500,000	3,000,000	5,000,000	Tin oxide, titanium dioxide zircon	
	$NaSb(OH)_6$	1,100,000	700,000			
Glass	Sb_2O_3	1,200,000	1,000,000	1,300,000	Tin oxide, titanium dioxide, arsenic trioxide, barite, fluorspar, manganese dioxide	
	$NaSb(OH)_6$	900,000	560,000			
Catalyst Antimony Oxide Acrylonitrile Polyesters Miscellaneous Antimony Chlorides	Sb_2O_3	2,500,000	2,100,000	4,200,000	Bismuth phospho-molybdate Various metal organics Numerous	
			
			
			
	$SbCl_3$	700,000	330,000			
	$SbCl_5$					
Color Stabilizer	Sb_2O_3	600,000	500,000	800,000	Other metallic oxides	
Dye Fixative	$K_2SbC_4H_4O_7 \cdot \frac{1}{2}H_2O$	300,000	100,000	150,000	Numerous	
	Sb_2S_3	300,000	210,000	200,000	Numerous	
Miscellaneous	Many		100,000	250,000	Numerous	
	8,600,000	12,400,000		
TOTALS						

*at current antimony oxide prices of \$1.07/lb.

Recommendation: The changing pattern of primary antimony usage, as indicated in the preceding demand data, requires a revised method of gathering and tabulating consumption statistics. The breakdown of consumption statistics should be revised to emphasize the functional usage of antimony. Changes should be made in the current mode of reporting consumption to the Bureau of Mines to reconcile differences in flame retardant versus other uses in various product categories. It is recommended that a flame retardant section, with subsections for plastic, rubber, pigment, etc., be added to the consumption categories for the Bureau's data.

Supply/Demand Balance

The demand for primary antimony is expected to increase at an annual rate of 5.8 percent over the 1969-1975 period. Cumulatively, over the 1969-1975 period, an additional 25,000 tons of primary antimony (over 1969 production levels) will be required to meet projected demand. If world demand closely parallels that of the United States, world production may rise to annual levels in excess of 90,000 tons by 1975.

Apparently, domestic antimony sources, as well as African and Bolivian sources, might be stimulated to meet expanding U.S. and world demand. In the near future, shortages in primary metal should be short term and cyclical. Over the next five years, known world resources appear adequate for domestic and world needs barring unanticipated international developments.

Increased usage of antimony seems assured. Increased production of antimony probably will be achieved in approximate balance with new needs, although temporary imbalances could result, pending the initiation of new or expanded production facilities.

Stockpile

Specifications for stockpiled metal and ore appear to be adequate. Approximately 95 percent of the antimony in the stockpile is in metal form and 5 percent is in ore. The relative amounts of ore and metal should be in the approximate ratio at which these items would be required in an emergency situation.

Most domestic oxide products use ore rather than metal as the preferred material.

Recommendation: With oxide demand growing five to ten times faster than metal demand, it is recommended that a higher percentage of stockpile material be in the form of ore and a decreased amount be in the form of metal.

II. INTRODUCTION

Antimony demand in the twentieth century has been characterized by acceleration during each of the major conflicts, World Wars I and II, the Korean conflict, and the Vietnam conflict; and by deceleration in the post-war years commensurate with ordnance and military hardware needs. The only long-term and prevalent demand factor in effect from the 1930's to the mid-1960's has been the growth in antimonial lead requirements in storage batteries, primarily in the expanding automotive market. Metallurgical applications, except ordnance, have provided the major portion of the continuous demand for the metal. However, the traditional pattern of antimony consumption is forecast to change significantly.

Flame retardant, catalytic, and other chemical uses of antimony will result in expanding demand for the metal. Metallurgical applications will assume a lesser role in future demand, particularly for primary antimony; secondary metal will provide a greater proportion of antimony requirements in metallurgical applications. New and expanding demand in chemical applications bodes well for the outlook for primary antimony and may serve to provide the orderly growth pattern that the antimony industry has sought. The availability of secondary metal may be affected by the shift to flame retarders and other chemical uses where the antimony may not be recoverable.

The changing pattern of demand for primary antimony, and the concomitant concern over the supply of antimony, prompted the Department of Commerce, Department of the Interior, General Services Administration, and Office of Emergency Preparedness, to request this Panel to assess the implication of technological change and usage trends on the supply/demand balance of antimony in applications utilizing, or likely to utilize, from the viewpoint of both essential civilian needs and military requirements. The adequacy of existing technical specifications for the stockpile material was also examined.

Prices and projections herein are based on inputs as of June 1970.

III. SUPPLY

A. World Resources

The United States in recent years has produced about 5 percent of its primary antimony requirements from domestic resources. Most of this production has been by-product recovery associated with smelting of lead-silver ores and various other lead smelter intermediate products. However, deposits valued chiefly for their antimony content have provided significant output during periods of high demand and elevated prices.

Known domestic resources of antimony are estimated to contain 110,000 tons of metal, about equally divided between the two major types of antimony deposits, simple and complex. The simple type of deposits contain small, discontinuous bodies of stibnite (Sb_2S_3) and occasional native antimony with associated silica and carbonate gangue minerals filling fissures and to a lesser extent replacing adjacent wall-rocks. Only small to negligible quantities of other metals are found. Such deposits are apparently hydrothermal in origin and commonly are associated with emplacement of granitic, dioritic, and monzonitic intrusives. Data on temperature and pressure indicate that relatively low temperature and near surface conditions prevailed during emplacement. Few of these simple deposits have significant vertical extent. In the second or complex type of deposit, antimony is associated with one or more other metals such as lead, gold, silver, zinc, copper, or tungsten. Antimony in these deposits may be present as stibnite, or more commonly in a variety of sulfantimonide minerals such as tetrahedrite. Because antimony is not the major value in most complex ores, its recovery is less responsive to price changes, and the supply of antimony is controlled by production rates set for the principal metals.

Within the United States, the Yellow Pine District, Idaho, is the outstanding example of a deposit that contains enough antimony so that its value exceeds that of other associated metals in the ore, i. e., gold and tungsten, when antimony

prices are high. Major production at the principal mine in the district began in 1932 and ceased in 1952, but plans have been announced to resume mining in the latter part of 1970. More than 75 percent of the Nation's production and a similar portion of its potential resources of 110,000 tons of antimony are accounted for between the Yellow Pine area and the Coeur d'Alene district, also in Idaho. In this latter area, especially in the ores of the "Silver Belt," tetrahedrite is a principal constituent. The antimony content generally ranges between 0.25 and 0.4 percent, and its recovery accounts for most of the 600 to 1,000 tons of recent annual production.

Some 70 mining districts in the United States contain potentially recoverable antimony. Almost all these districts are in the western United States in a north-trending belt lying between 111° and 122°W longitude. Further, within this belt, two-thirds of the deposits of the simple type are localized in the western half of the belt, whereas only one-third of the complex deposits are west of 117°. This regional zoning pattern is further associated with the distribution of quicksilver deposits, which tend to occur in the western part of or west of the antimony belt.

World resources of antimony have been estimated at more than 4 million tons, with China accounting for about half of the known reserves. Bolivia, South Africa, Russia, and Mexico together account for about a third of the known resources, and Turkey, Australia, United States, Yugoslavia, Peru, Algeria, Canada, Czechoslovakia, and Hungary for the remainder. Recent increases in the price of antimony have stimulated the search for new antimony supplies and intensified development of known lower grade deposits. Outside of China, the only sizable deposits that have been minable on a continuous moderately large scale are in South Africa and Bolivia. Possibly the deposit at Yellow Pine, Idaho, will again prove to be exploitable.

On a worldwide basis, known resources appear to be adequate to support present levels of production and sustained increased prices might be expected to result in increased levels of production.

B. World Production

Over the past forty years world production of antimony has increased approximately fourfold in a generally erratic pattern. From a low point of approximately 18,000 tons in 1931, world production expanded continuously to approximately 58,000 tons in 1943, reached a low of approximately 30,000 tons in 1946, and subsequently increased in a cyclical pattern to a modern high of 69,400 tons in 1965. The erratic nature of world production is attributable to the economic cycles commensurate with pre- and post-war activity and to the demand for this critical material in time of war.

China supplied approximately 63 percent of the total world production from 1925 to 1937. The Japanese invasion of eastern China in 1937 had a significant impact on the antimony production capability of China. However, the decrease in China's contribution to world production was compensated by expanded production in North and South America and, to a lesser extent, in Europe. These continental shifts in producing capability persist today. Africa's contribution to world production became significant in the late 1940's.

A more recent perspective of world production of antimony is given in the production statistics of Table 3 listing world production for the 1958-1968 period, compiled by the Bureau of Mines. The major producers of antimony in 1968 were the Union of South Africa (18,500 tons), mainland China (13,200 tons, estimated), Bolivia (12,200 tons), and the USSR (7,000 tons, estimated). Nineteen hundred and sixty-eight was the first year in which the African continent surpassed Asia in antimony production, and the second year in which South Africa led all countries in antimony production.

The accuracy of production estimates for the Sino-Soviet block remains questionable. The antimony production of the Bloc countries, as given in Table 3, decreased from 24,900 tons in 1958 to 21,400 tons in 1968. In a decade of nominal prosperity, this trend could indicate depleted reserves, redeployed mining resources, or errors in available statistical data.

In 1969, plans were announced for expansion of South Africa's antimony production capability. The expansion of production capacity to some 25,000-30,000 tons annually indicates South Africa's dominance in future world supply of antimony. Probably, Bolivia will remain the world's second largest supplier of antimony.

The production of Oceania (primarily Australia) decreased sharply in the early 1960's and, by 1963, was reported to be 83 short tons of metal equivalent. However, production levels increased to over 1,000 tons annually in 1964 and subsequent years. Current plans for expansion would double or treble Oceania's output. Forward contracts commit expanded output to Japanese smelters and, subsequently, to Japanese and western European markets.

C. Domestic Supply

The United States depends almost totally upon imports to satisfy domestic primary antimony requirements. Although substantial quantities of antimony have been produced from domestic mines in the past, recent supply from domestic sources has been quite limited. With imports as the most important source of new supplies, the cogent factors are sources of supply and availability of required material.

Antimony mine production and shipments in the United States during the past ten years are summarized in Table 4. Antimony production in 1968 was limited to cathode antimony produced at the electrolytic plant of the Sunshine Milling Company in Idaho. The source of the metal was silver ore from the Sunshine Mines and adjacent properties.

TABLE 3. World Production of Antimony (Short Tons Metal)

	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
United States	705	678	635	689	631	645	632	845	927	892	856
Mexico	3,029	3,622	4,664	3,978	5,257	5,320	5,279	4,917	4,868	4,121	3,819
Other N. A.	477	926	945	737	998	832	796	651	718	667	865
Total N. A.	4,211	5,226	6,244	5,404	6,886	6,797	6,707	6,413	6,513	5,680	5,540
Bolivia	5,818	6,065	5,872	7,430	7,331	8,337	10,648	10,615	11,760	12,432	12,188
Peru	964	793	901	870	575	815	752	713	741	700	739
Other S. A.	11										
Total S. A.	6,793	6,858	6,773	8,300	7,906	9,152	11,400	11,328	12,501	13,132	12,927
Czechoslovakia	1,800	1,800	1,800	1,800	2,200	2,200	1,300	1,300	1,300	1,200	1,200
U. S. S. R.	6,600	6,600	6,300	6,300	6,600	6,700	6,700	6,800	6,900	7,000	7,000
Yugoslavia	1,835	2,514	2,657	2,715	2,966	2,933	3,008	3,051	2,916	2,533	1,935
Other Europe	971	1,049	1,157	1,134	1,311	989	1,081	967	954	958	1,234
Total Europe	11,206	11,963	11,914	11,949	13,077	12,822	12,089	12,118	12,070	11,691	11,369
Morocco	203	252	358	406	449	744	1,720	2,425	1,480	1,753	1,336
South Africa	7,904	13,619	13,537	11,804	11,697	12,410	14,200	13,901	12,534	13,666	18,511
Other Africa	1,257	1,239	986	788	210	66	49	271	103	129	123
Total Africa	9,364	15,110	14,881	12,998	12,356	13,220	15,969	16,597	14,117	15,548	19,970
China	16,500	16,500	16,500	16,500	16,500	16,500	16,500	16,500	16,500	13,200	13,200
Turkey	1,687	1,380	1,507	1,502	1,962	1,981	3,631	3,896	3,396	2,244	3,446
Other Asia	548	776	762	532	422	1,023	1,857	1,547	1,442	1,345	384
Total Asia	18,735	18,656	18,769	18,534	18,884	19,504	21,968	21,943	21,338	16,789	17,030
Oceania	775	703	172	132	74	83	1,250	1,057	1,088	1,009	931
Total World	51,084	58,516	58,753	57,317	59,183	61,578	69,403	69,456	67,627	63,849	67,767

Source: U. S. Bureau of Mines.

TABLE 4. Antimony Mine Production and Shipments in U. S.
(Short Tons)

Year	Antimony Concentrate Quantity	Antimony	
		Produced	Shipped
1958	4,309	705	382
1959	4,671	678	146
1960	4,256	635	1,086
1961	4,245	689	1,646
1962	3,941	631	732
1963	3,540	645	503
1964	3,296	632	789
1965	4,711	845	848
1966	5,582	927	930
1967	5,402	892	828
1968	5,263	856	941

The quantities of antimony produced from domestic mines have little effect upon the total supply available in the United States. This apparent lack of the natural antimony resource underlines the importance of exploration and development of presently known sources.

D. Production of By-Product Antimony

By-product antimony is recovered in the refining of lead bullion produced from ores mined primarily for their lead content.

Actual figures on production of by-product antimony are not published, but a realistic estimate can be made for U. S. production. The following producing plants are included: Asarco Refineries at Omaha, Nebraska, and Selby, California; Bunker Hill Refinery at Bradley, Idaho; and U. S. Smelting Refinery at East Chicago, Indiana.

Current antimony production from these refineries is estimated at 3,000 short tons annually. This figure includes antimony recovered from lead bullion produced from domestic and imported concentrates and is a small portion of total U. S. production.

During periods of over-supply of lead, speculations on the trends in lead mining having suggested that a potential economic advantage might accrue if production in the Missouri "lead belt" were accelerated in preference to ores from many of the western mining districts. The supposed advantage arises mainly from the larger scale of individual mining operations in the Missouri area and is aided partially by the lower refining costs for lead from the "cleaner" (i. e., fewer associated by-product metals) ores produced in Missouri. The ores from the western mining districts contain more associated metals, including antimony and also significant amounts of silver. Although smelting costs for their lead may be higher, the value of the by-products is also greater. Projected increases in both demand and price for these associated metals, particularly silver, effectively cancel the supposed advantage. If such a shift were to become a reality, the decrease in output of antimony would be significant.

With regard to the rest of the Free World, any estimate of by-product recovery is highly theoretical. Using published figures on lead refinery capacity, presumably up to 15,000 tons of antimony could be produced as a by-product of lead bullion.

E. Imports

Approximately 95 percent of total U.S. primary antimony needs are supplied by imports. Table 5 shows imports of antimony ore, metal, and oxide, and also lists the most important source countries. Over the past ten years, South Africa has become the major source of imported antimony ore for domestic use. Prior to 1966, Mexico had been the primary source of imported ore. In 1968 and 1969, the Republic of South Africa supplied approximately 50 percent of domestic antimony imports with the balance supplied about equally by Bolivia and Mexico. Major sources of metal imports in 1968 were Yugoslavia, the United Kingdom, Mexico, and Belgium/Luxemburg. Important sources of antimony oxide in 1968 were the United Kingdom (1,848 tons), Belgium/Luxemburg (1,108 tons), and France (721 tons). A grand total of 17,343 tons of ore, concentrate, metal, and oxide were imported in 1968, and a (preliminary) total of 17,085 tons were imported in 1969.

F. Smelter Production

The class of material produced at primary antimony smelter sites in the United States is shown in Table 6 for the ten-year period 1958-1968. Over the past five years, the total output of domestic smelters has averaged about 13,000 short tons antimony content. This is approximately two-thirds of total primary antimony requirements with the balance being supplied by imports. Smelters operate primarily with imported ores; their major products are oxide, metal, or antimonial lead. Almost all the Mexican ore is converted to metal; most of the Bolivian and South African ore is converted to oxide.

G. Secondary Production

The last major source of antimony in the United States is secondary production. It contributes 30-60 percent of total annual supply in the United States, and in 1968, supplied approximately 55 percent of domestic requirements.

TABLE 5. U. S. Imports of Antimony

Country	Antimony Ore (Short Tons Metal)								
	1960	1961	1962	1963	1964	1965	1966	1967	1968
Bolivia	974	362	830	982	2,128	2,304	3,470	2,439	2,521
Mexico	2,699	3,411	4,072	3,999	3,937	3,770	3,868	3,018	2,606
South Africa	2,291	2,670	3,668	3,971	3,951	3,292	4,006	4,117	5,196
Other	491	270	32	832	660	994	1,116	943	291
TOTAL	6,455	6,713	8,602	9,784	10,676	10,360	12,460	10,517	10,614
Antimony Metal (Short Tons Gross)									
TOTAL	90	4,912	4,740	5,696	3,402	2,719	2,805	2,681	2,764
Antimony Oxide (Short Tons Gross)									
TOTAL	-	1,980	2,910	2,089	3,131	2,178	5,383	5,098	4,801

TABLE 6. Primary Antimony Processed in the U. S.
(Short Tons, Antimony Content)

Year	Class of Material Produced					
	Metal	Oxide	Sulfide	Residues	By-product Antimonial Lead	Total
1958	2,833	3,825	84	319	1,496	8,557
1959	2,667	4,411	70	430	1,170	8,748
1960	3,665	5,188	60	385	656	9,954
1961	4,558	4,609	84	355	1,723	11,329
1962	4,407	4,788	53	366	2,113	11,727
1963	4,160	5,983	76	392	1,506	12,117
1964	4,418	6,748	53	447	1,692	13,358
1965	4,216	6,485	94	205	1,389	12,389
1966	4,567	7,794	126	219	1,833	14,539
1967	4,002	6,612	71	249	1,532	12,466
1968	3,617	6,518	133	417	1,804	12,489

Most secondary antimony is recovered from lead, tin, or lead scrap (discarded storage batteries). Quantities are also recovered from Babbitt metal, Type metal, and lead dross. The recovery process is carried out in secondary smelters, remelters, refiners, and at primary lead refineries. Depending upon the degree of purity of the scrap, these plants either resmelt the scrap or produce a specification material through the addition of lead, tin, or antimony.

Table 7 lists secondary antimony production in the United States over the past ten years. Table 8 lists by-product antimony derived from lead smelting and normally converted to a lead-antimony alloy.

All antimony derived from secondary sources is normally consumed in secondary alloy (PbSb) production.

IV. CONSUMPTION AND PROJECTED DEMAND

A. Metallurgical Applications - Batteries

The lead-acid storage battery provides starting, lighting and ignition power for all automotive, truck, bus, marine and for many aircraft applications. It is used for motive power for industrial trucks, submarines and golf cars, and for a broad range of emergency standby power and lighting systems. This type of battery is heavily dependent on lead-antimony alloys for structural and current carrying components resistant to the sulfuric acid electrolyte. Usage trends for the period 1960-1970 are shown in Figure 2. The antimony content associated with these alloy tonnages is shown in Figure 3. An overall growth of about 3 percent per year characterizes this period.

The antimony content of the alloys varies with the type of component and the use for which the battery is designed. Antimony contributes the following:

TABLE 7. Secondary Antimony Recovered in the U. S.

Year	Short Tons, Antimony Content
1958	19,515
1959	NA*
1960	20,104
1961	19,466
1962	19,362
1963	20,803
1964	22,339
1965	24,321
1966	24,258
1967	23,664
1968	23,699

*NA = Not available.

TABLE 8. By-product Antimonial Lead Produced
at Lead Refineries in the U.S.

Year	Short Tons, Antimony Content
1958	2,803
1959	1,924
1960	1,575
1961	1,894
1962	2,249
1963	1,890
1964	1,995
1965	1,984
1966	2,119
1967	1,717
1968	2,007

Figure 2. U.S. Storage Battery Industry Antimonial Lead Consumption—Dollar Value

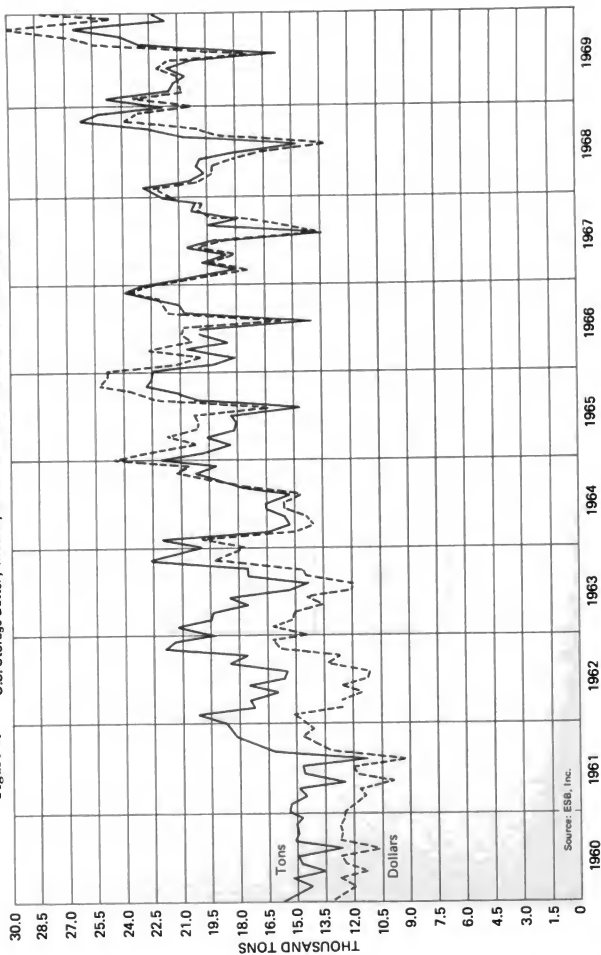
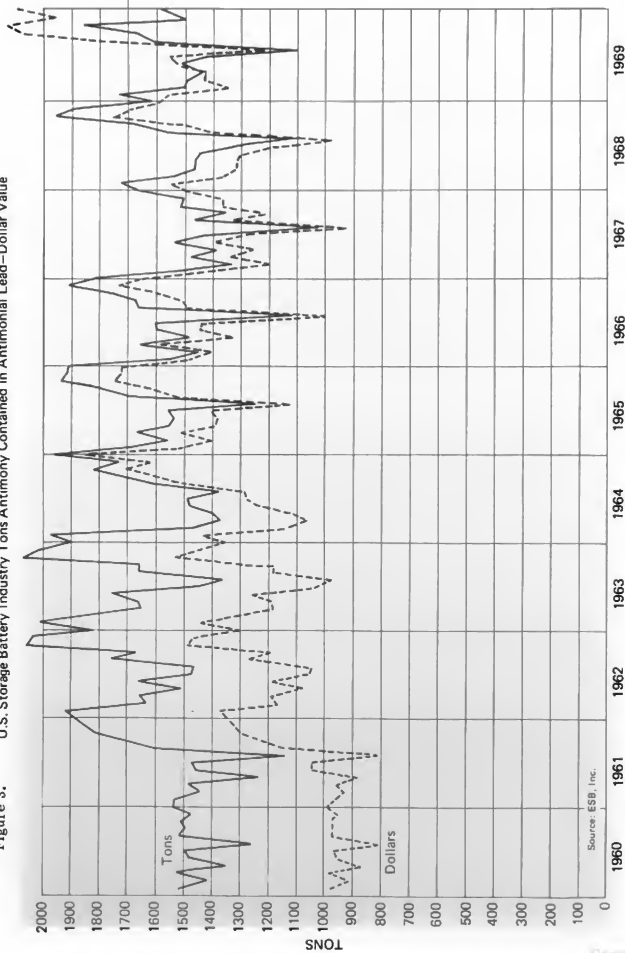


Figure 3. U.S. Storage Battery Industry Tons Antimony Contained in Antimonial Lead-Dollar Value



1. Fluidity for high-speed casting of thin sections
2. Strength for resisting creep and fatigue in service
3. Electrochemical stability for heavy-duty cycling of battery plates

The use of calcium in place of antimony for strengthening alloys in batteries for standby power installations has become common. However, these comprise only a portion of the "industrial battery market" which, over the period 1960-1970, used only 10.9 percent of the total storage battery lead requirements.

Previously, when antimony prices were high, nonantimonial alloys were not feasible economically in the automotive starting-lighting-ignition (SLI) market because of the dependence of high rate gravity-fed permanent mold "grid" casting equipment on the fluidity and solidification characteristics of the antimonial alloys. Reduction in antimony contents has progressed from optimum eutectic levels of about 11 percent to a current estimated average of about 5.5 percent. The 5.5 percent average level for antimony is derived from reports of various manufacturers to the Battery Council International Headquarters. The present tonnage in all battery applications is estimated at 14,800 tons by the Council.

At antimony price levels about \$1.50 per pound, there will be increasing attempts to reduce antimony levels further, and the average antimony level is expected to fall to about 4-1/2 percent within five years, even possibly as low as 3-1/2 percent.

Antimonial lead for storage batteries is derived mainly from secondary sources, primarily, the reuse of battery scrap. About 10 percent of the antimony content is lost in smelting. Accordingly, primary antimony is required to make

up losses and to provide for market growth. In addition, approximately 20 percent of the batteries produced are not recycled.

Projection of antimony usage through 1975 is shown in Tables 9, 10, and 11 and is based on the assumptions indicated.

The projected price of antimony will heavily influence the development effort and capital investment which will be devoted to the substitution of nonantimonial alloys as indicated in Table 11. Due to the extreme difficulty in processing, it is expected that Table 10 more nearly reflects the future situation through 1975. However, should the price remain above the \$1.80 level, there is a possibility that totally new processing systems can be developed to permit the use of nonantimonial alloys in noncycle applications, which would make achievement of the 3.5 percent average level possible by 1975.

The Antimony Panel has selected Table 10 as most clearly representing antimony requirements in battery applications over the coming five years. Supplemental data in support of this forecast appear in correspondence from C. H. Allen, Executive Secretary, Battery Council International.

Information regarding antimony requirements by the lead-acid battery industry was requested from ten battery manufacturers in the United States. These data were used to plot Figures 4, 5, and 6.

Figure 4 was plotted using the average of quantities of antimony reported used in SLI and equivalent, or similar types of batteries. The battery curves on this graph were projected on the basis of trends indicated for the years 1960 through 1969. Forecasts from several sources were used to modify the historical trends indicated since 1969. The forecast takes into account the increasing use of batteries similar to SLI types and sizes for new service applications, such as recreational vehicles and equipment, boats, personnel carriers, etc.

TABLE 9. Projected Antimony Consumption of Storage Batteries Through 1975

Assumptions						
(1) 5.5 percent 1970 average antimony content. (2) Straight-line projection of total lead alloy usage in storage batteries assuming continuation of historical 3 percent per year increase. (3) Reduction to 4.5 percent average antimony content by 1975.						
	1970	1971	1972	1973	1974	1975
Lead-antimony alloy, short tons x 1,000	270	278	286	295	304	315
Total antimony requirement, short tons	14,800	14,700	14,575	14,450	14,325	14,200
Primary antimony requirement, short tons	6,200	6,050	5,975	5,925	5,875	5,825

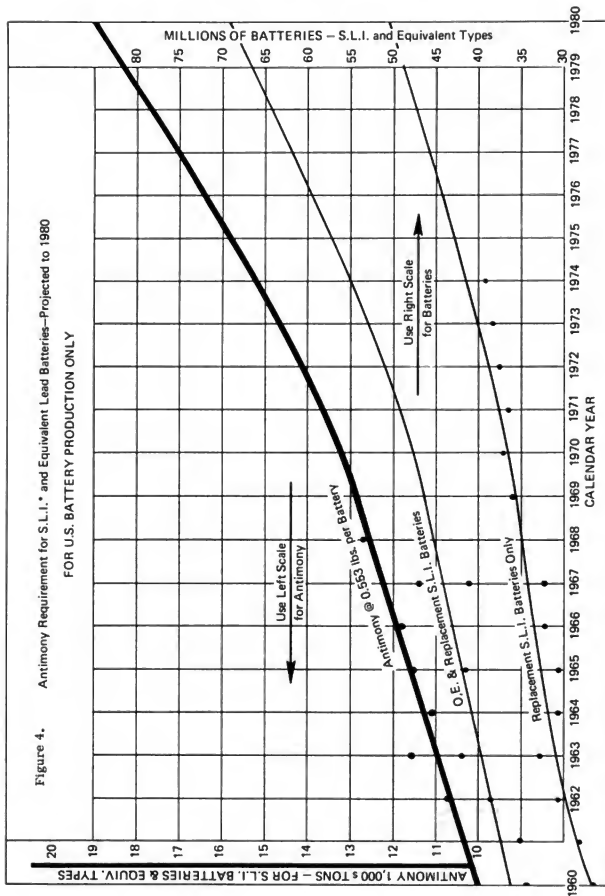
TABLE 10. Projected Antimony Consumption of Storage Batteries Through 1975

Assumptions						
(1) 5.5 percent 1970 average antimony content. (2) Projection of total lead alloy usage based on increased electric vehicles and devices to give approximately 5 percent per year increase. (3) Reduction to 4.5 percent average antimony content by 1975.						
	1970	1971	1972	1973	1974	1975
Lead-antimony alloy, short tons x 1,000	270	285	300	315	330	360
Total antimony requirement, short tons	14,800	15,100	15,400	15,650	15,900	16,200
Primary antimony requirement, short tons	6,200	6,610	6,750	6,800	6,900	7,080

TABLE 11. Projected Antimony Consumption of Storage Batteries Through 1975

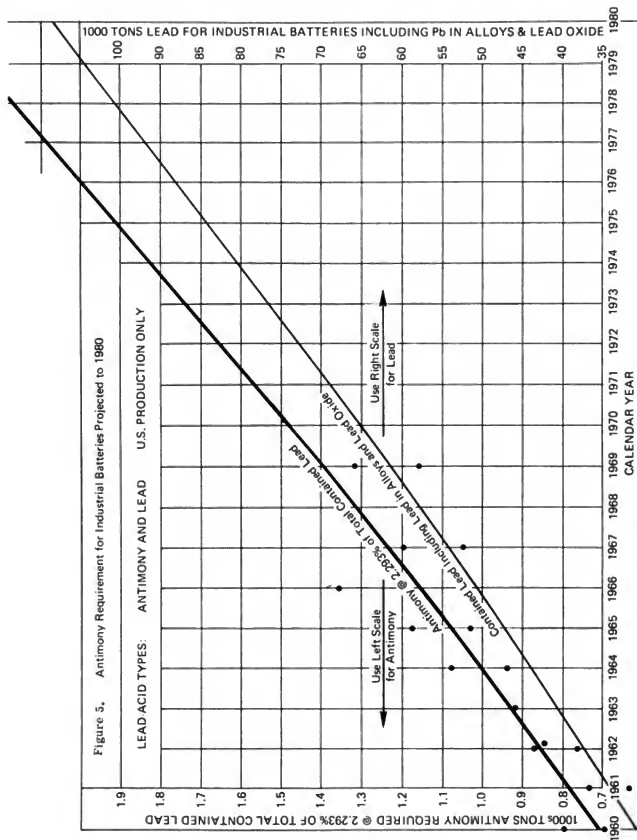
Assumptions						
(1) 5.5 percent current average antimony content. (2) Straight-line projection of total lead alloy usage in storage batteries: 3 percent per year increase - same as Table 9. (3) Reduction to 3.5 percent average antimony content by 1975 based on partial substitution of nonantimonial alloys.						
	1970	1971	1972	1973	1974	1975
Lead antimony alloy, short tons x 1,000	270	278	286	295	304	315
Total antimony requirement, short tons	14,800	14,100	13,350	12,600	11,800	11,025
Primary antimony requirement, short tons	6,200	5,200	4,850	4,550	4,150	3,900

Figure 4. Antimony Requirement for S.L.I.* and Equivalent Lead Batteries—Projected to 1980
FOR U.S. BATTERY PRODUCTION ONLY

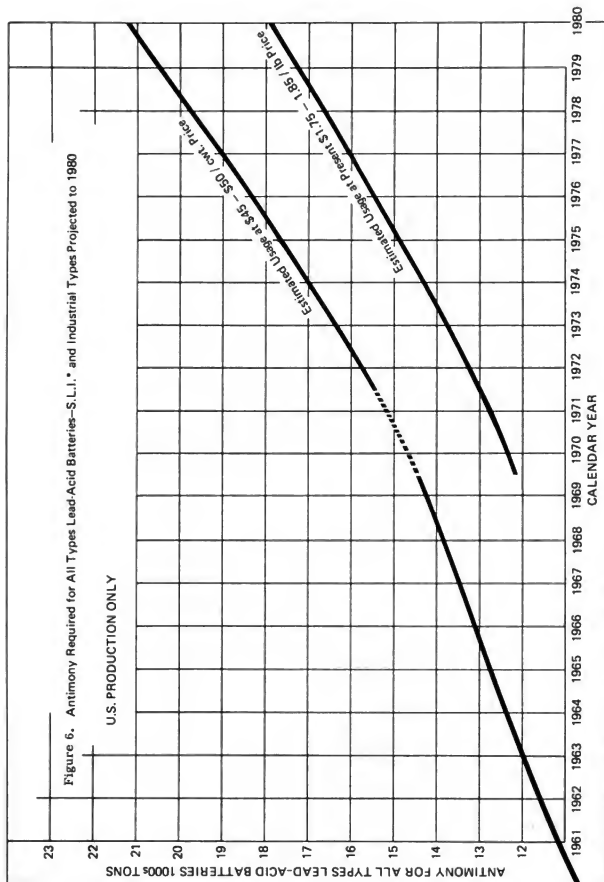


BATTERY COUNCIL INTERNATIONAL, MAY 26, 1970

*S.L.I. = Starting-Ignition



BATTERY COUNCIL INTERNATIONAL, MAY 26, 1970



From the above survey, the antimony curve on Figure 4 projects antimony requirements for SLI-type batteries on the basis of 0.553 pounds used per average battery. This amount probably would be reduced if the present price level continues. The amounts reported ranged from less than 0.3 pounds to 0.7 pounds per average battery. However, manufacturers using more than 0.4 pounds are striving to lower the quantity of antimony used. At the present price level, antimony for SLI-type batteries may drop from the average of 0.553 pounds shown to 0.450 pounds, or lower within the next two or three years. In order to overcome some of the production difficulties encountered with low antimony, reportedly the quantity of arsenic and tin are being increased, although not on a pound for pound basis.

Figure 5 relates antimony to the amount of lead used by the industrial battery industry. Reports received gave the lead including oxide used by the major manufacturers of industrial batteries in the United States. Data were also received concerning the amount of antimony used by several of the major manufacturers. Because of the manner in which these reports were received, the antimony was related to the sum of lead in alloys and lead in lead oxide used.

The lead curve of Figure 5 was projected on the basis of quantities reported used during the years 1960 through 1969. The projection was modified by some anticipated increases for industrial type batteries. As indicated, the antimony curve was based upon 2.293 percent of the total contained lead in batteries being manufactured by several major manufacturers. This accounted for the absence of antimony in some industrial-type batteries. Information was not available on how much the antimony content of industrial batteries could be lowered if the present price level were to persist.

Figure 6 shows the sum of the estimated antimony requirements as described for Figures 4 and 5.

B. Metallurgical Additive in Products Other Than Batteries

The U.S. usage of antimony in this whole area is currently in the neighborhood of 1,900 short tons per year. This is only one-third of the primary antimony used in the production of batteries and less than 10 percent of the total U.S. consumption of primary antimony.

An individual breakdown of uses follows:

1. Bearing Metals. Current consumption is 750 tons of antimony annually. These metals run between 4 and 15 percent antimony content with an average of 10 percent. This market has been losing ground steadily over the past five years, 1969 usage being about 50 percent of 1964. This drop has been occasioned by large-scale switching to radically different bearings rather than a substitution for antimony as an additive. By 1975, consumption could be expected possibly to be as low as 400 tons.

2. Type Metal. Type metal contains between 4 and 23 percent antimony content, averaging 12 percent. In 1969, consumption of antimony in type metal was estimated at 400 tons. This consumption has been relatively constant over the past five years, and no great change is forecast by 1975. To date, no particular substitution has been evident. Efforts are now being made to lower the antimony content in response to rapid price increases. A rather large volume of material is recycled in this industry. Accordingly, annual requirements are limited largely to replenishing needs.

3. Solder. Today's usage is approximately 225 tons. Solder contains between 0 and 2 percent antimony, averaging 0.5 percent. Consumption in this area has not varied greatly over the past five years, and no great change is foreseen by 1975. Because of the low percentage contained in the final product, large changes in consumption of solder would have to occur to affect antimony usage appreciably.

4. Cable Covering. Current consumption is 150 tons in a metal containing between 0.8 and 1.0 percent antimony. In the last five years, this tonnage dropped greatly because aluminum and plastic coverings were substituted for lead sheathing. The remaining uses of lead covering are considered necessary, and their consumption by 1975 should remain constant.

5. Ammunition. Consumption is estimated at 150 tons per year. Lead for ammunition contains between 0.5 and 8.0 percent antimony, averaging 4.0 percent. Obviously, this market has varied with the hostilities in effect at any particular time. There has been no substitution for antimony so far as military usages are concerned, but the substitution of steel shot for lead in shotgun shells is a very good possibility. Conservationists strongly believe that ducks are ingesting spent shot from the bottom of lakes and ponds and are developing lead poisoning. A decline in this usage of antimony is forecast; therefore, consumption by 1975 should be less than 100 tons.

6. Miscellaneous. This category includes sheet, pipe, castings, collapsible tube, foil, etc. Current consumption is estimated at 225 tons. This figure has been relatively steady over the last five years. Because of the variety of industries involved, no great change can be forecast by 1975.

In conclusion, due to the relatively small volume of antimony consumed in all these areas, little research or development work could be justified.

C. Chemical Uses - Flame Retarders

Antimony is used extensively as a flame retarder in adhesives, paint, paper, plastics, rubber, textiles, and other flammable materials, and acts as a synergist with halogens, since it is seldom effective alone. Although many antimony chemicals are mentioned in the literature as being effective, antimony trioxide is the compound most commonly used as a flame retarder.

In 1969, an estimated 6,700 short tons of antimony were used as flame retarders.*² Demand for flame retarders could increase sharply in the next five years, but accurate forecasting of antimony flame retarders is impossible because of these strong conflicting influences:

- Legislative and other regulatory pressure to increase use of flame retarding materials and to improve performance of those already in use.
- The acute shortage of antimony in 1970 and the resulting high prices that stimulated extensive efforts to develop substitutes.

1. Impact of Legislation and Regulations. Government, insurance, and industry regulations are expected to force consumption of flame retarders to grow rapidly in the next five to ten years.

Government requirements are imposed in several ways. The Federal government is a large consumer and, by specifying the performance of materials it purchases, it has established flame retarding requirements for a variety of items such as tarpaulins, electric cables, lifeboats, and space capsule furnishings.

Government agencies also regulate industries and practices within them. Under their authority, the Federal Aviation Administration regulates the flammability characteristics of aircraft cabin furnishing,³ and is also

*There are conflicting estimates of antimony flame retarder consumption. Modern Plastics (Sept. 1969) estimates that 14,000,000 lbs. of antimony trioxide were used as flame retarders in plastics during 1968, and 16,000,000 lbs. in 1969. These figures are equivalent to 5,840 and 6,680 short tons of antimony, respectively. These are considerably higher than Bureau of Mines estimates of 6,436 and 4,830 (preliminary) for consumption in all flame-retarding categories. During preparation of this report, it was estimated from various industrial sources that all flame-retarding use in 1969 totalled 6,680 short tons of antimony.

preparing a regulation for controlling smoke-evolution characteristics.⁴ The Federal Highway Administration has proposed a similar standard for motor vehicle interior materials⁵ to be effective on January 1, 1971.

The proposed new Motor Vehicle Standard will be based on an investigation by IIT Research Institute.⁶ IITRI tested over 200 different vehicle interior materials and rated them against a proposed standard. About 20 percent of all materials tested failed to meet the proposed standard. From the report, there is no way to ascertain directly how much additional antimony will be required for flame retarders when the standard becomes effective. However, the standard will apply to much of the nearly one billion pounds of plastics used in 1970 model vehicles, and antimony oxide could be used in a major portion of the 433 million pounds of ABS, PE, PP, and PVC used.⁷ Over half the tested vinyl fabric samples failed the proposed standard; therefore, it is likely that more antimony oxide will be needed there. If all these materials were substandard, the amount of antimony oxide required to make all these specific plastics flame retarding would total 35,000,000 pounds or 14,100 tons of contained antimony. Only a small portion of this antimony oxide is expected to be needed to meet the new standard because some materials already meet it, others will not be covered by the standard, and other flame retarders will also be used in place of antimony oxide. However, even a 5,000,000-pound increase in demand for antimony oxide would represent a 30 percent increase over present consumption of antimony flame retarders.

The Flammable Fabrics Act⁸ directs the Secretary of Commerce to set appropriate flammability standards to protect the public from unreasonable risk of death, injury, or property loss due to fire involving fabric and related materials. A proposed standard was issued on December 17, 1969, covering carpets and rugs. Antimony chemicals are used as flame retarders in carpet backing and underlay, and demand has already increased for these applications.

The Secretary of Commerce has recently moved to establish standards of flammability in children's wear and other wearing apparel. Antimony flame retarders are not generally used in textiles except for military fabric⁹ or other heavy fabrics because they tend to make the fabric stiff and coarse. A standard is expected to be issued eventually covering flammability of mattresses, and it should create another potential demand for antimony oxide for foam rubber and fabrics.

Another legislative act influencing use of flame retarders is the "Federal Coal Mine Health and Safety Act,"¹⁰ which directs the Secretary of Health, Education, and Welfare and the Secretary of the Interior to set health and safety standards to protect the nation's coal miners. A similar act, the "Occupational Safety and Health Act of 1969," applies in a similar manner to other occupations. Under these acts, flammability standards for equipment and buildings can be established.

The most important government requirements for flame retarding materials are found in building codes that set standards for various classifications of materials used in construction. Building codes are established by local or state governments or by industry associations. The Federal Housing Administration Multifamily Minimum Property Standards are examples of Federal Standards similar to building codes. Together with insurance requirements, codes restrict the use of flammable materials of construction, particularly in institutional, commercial, and industrial construction. Many new plastics products could not have been introduced to the construction industry until flame retarders were formulated that permitted compliance with building code and insurance standards. Some of the most important building codes are listed below:

National Building Code
American Insurance Association, New York, New York
Uniform Building Code
International Conference of Building Officials
Los Angeles, California

Southern Standard Building Code
Southern Building Code Congress
Birmingham, Alabama

Basic Building Code
Building Officials Conference of America
Chicago, Illinois

Modern Standard Building Code
Midwest Conference of Building Officials
Chicago, Illinois

National Building Code
Canada

Insurance requirements are set by individual underwriters with guidance from their industry authorities. Testing and approval Services are offered by Factory Mutual Engineering Corporation (for Associated Factory Mutual Insurance Companies) and Underwriters' Laboratories (for Fire Insurance Association Companies). The services of these organizations are available to manufacturers of building materials or other products.

2. Consumption in Flame Retarders. The Bureau of Mines reports the industrial consumption of antimony quarterly, by class of material. For 1968, the last full year for which final figures are available,¹¹ the following flame retarding use of antimony was indicated:

Product	Antimony Content (Short Tons)	Antimony Trioxide Equivalent (Lbs.)
Flameproofing chemicals and compounds	2,774	6,640,000
Pigments	859	2,060,000
Plastics	2,318	5,550,000
Rubber products	440	1,080,000
Other (adhesives)	45	105,000
Total	6,436	15,435,000

Source: U.S. Bureau of Mines Mineral Industry Surveys

Note that "Plastics," "Rubber products," and "Adhesives" (not listed separately but reported as part of "Nonmetal products - other") have been included with "Flameproofing chemicals and compounds," because antimony is used in these materials only as a flame retarder, except for very minor amounts.

The antimony reported as pigments conceivably could be included under flame retarding use, since only minor amounts of antimony are used primarily as pigments, although antimony chemicals are used as flame retarders in paints and coatings. When all the above product categories are considered flame retarding uses, the total is in fair agreement with other estimates. However, industry estimates of consumption in some product categories differ widely from the Bureau of Mines' figures, and differences will be commented on later in this report.

The pattern of consumption for the 1964-1969 period, reported by the Bureau of Mines, is shown below:

Total Antimony Flame Retarder Use
(Short Tons Sb)

<u>1964</u>	<u>1965</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>1969</u>
4,620	4,812	7,154	6,892	6,436	6,700 (est.)

The sudden increase in consumption in 1966 and 1967 is attributed to heavy military purchases of flame retarding fabrics for the Vietnam War. Consumption in 1969 is believed to be lower than actual demand because supplies were restricted. Consumption may drop sharply in 1970 because high prices are forcing users to seek substitutes or supplements for antimony flame retarders. Because of these complications, no clear trend in consumption is obvious from the historical data.

Antimony trioxide is the primary antimony flame retarding chemical used, although several proprietary antimony chemicals are also sold. Some of the proprietary products are claimed to be as effective as antimony trioxide, and would use less antimony. This, then, represents a means of extending the supply of antimony. The nominal antimony content of three of these materials varies from 40 percent to 70 percent, compared with 83 percent in antimony trioxide. Other materials used as substitutes or supplements for antimony will be mentioned later.

a. Fabrics. The oldest major use of antimony flame retarders is to protect military fabrics, such as tarpaulins, uniforms, tents, etc. For this use, antimony oxide, sometimes in combination with other metal oxides, such as titanium dioxide or iron oxide, is mixed with chlorinated paraffins, resins, or solvents and coated onto fabrics. Borates, such as barium metaborate, are claimed to serve as an afterglow suppressor and as a replacement for up to 40 percent of the antimony oxide normally required. This type of flame retarder was used extensively on Vietnam War materials during 1966 and 1967 and accounts for the sharp increase in flame retarder use in those years.

In the past, the primary demand for flame retarding textiles was for military and other special uses (some work clothes, tents, awnings, drapes and curtains for public or institutional use, etc.). Recently, due to legislation and publicity and also due to the development of new finishes, which preserve the cloth-like feel and appearance of textiles, demand for flame retarding textiles has expanded. The antimony-based treatments used for FWWMR (Fire, water, weather, mildew resistant) finishes have been supplemented with phosphorous-nitrogen- and halogen-based materials. The most important classes of durable finishes include: antimony oxide/chlorinated organic systems; antimony oxide/PVC/Tetrakis (hydroxymethyl) phosphonium chloride (THPC) types, THPC/amide finishes, aziridinyl phosphine oxide (APO)/thiourea systems; phosphonitrilic chloride types, and an n-methylol dialkyl phosphonopropionamide system.

In 1969, antimony based flame retarding finishes were less expensive than other durable finishes, but tend to make textiles feel stiff and look coarse. At 1970 antimony oxide prices (as high as \$3.20 per pound for imported oxide), other systems may have a cost advantage as well. To compete in the growing textile market, antimony chemicals must offer a cost advantage. Numerous nonantimony commercial flame retarders are offered for use on fabrics.¹² With the variety of materials available to do the job, antimony flame retarders have lost much of their strategic value for treating military fabrics, and a decline in their use is to be expected.

b. Plastics. Polyvinylchloride represents the major single plastic use for antimony flame retarders. An estimated 5,000,000 pounds of antimony oxide are used annually in PVC sheeting, film, and coatings. No supplemental halogen source is required because the PVC contains sufficient chlorine. In fact, rigid PVC does not generally require antimony oxide, but antimony oxide is added to plasticized PVC to compensate for the flammable plasticizer and other additives. Plasticized PVC can also be made flame retarding by substituting phosphate ester plasticizers (such as TCP, tricresyl phosphate) for the more flammable phthalic acid ester plasticizers (such as DOP, dioctyl phthalate). Chlorinated paraffins are also used as secondary plasticizers to reduce the need for flammable DOP. Phosphate ester plasticizers cost about \$0.17 per pound more than DOP, and 10-15 parts per hundred of resin (phr) are generally substituted for a like amount of DOP, adding about \$1.70 to \$2.55 to the cost of a compound. Antimony oxide is required at the 2-5 phr level, so would add \$1.00 to \$2.50 to the compound cost at an antimony oxide price of \$0.50 per pound or \$2.00 to \$5.00 at \$1.00 per pound.

Clearly, antimony oxide is more costly to use than TCP at an antimony price of \$1.00 or more per pound, so the phosphate plasticizers

are now preferred from an economic standpoint. However, they tend to "spew" and impart poorer low-temperature flexibility and heat stability than DOP, so the decision to substitute them for antimony oxide is not simple. Many firms may prefer using antimony oxide to developing new formulations, conducting expensive reapproval testing, and risking a change in a successful formulation. There have also been periodic shortages of cresylic acid that have restricted use of TCP, the largest volume phosphate ester plasticizer. Despite the economics, manufacturers of PVC products are expected to consume growing amounts of antimony oxide if prices remain around \$1.00 per pound.

One major use of antimony flame retarders for which there does not appear to be a substitute is in ABS, polypropylene, and polyethylene. Here, antimony oxide is used with a variety of halogen sources. At least 6 phr of antimony oxide are used in polyethylene and about 15 phr in ABS and polypropylene. Together, these plastics represent about 20 percent of the antimony flame retarder market. As antimony oxide increased in price, it caused the price of flame retarding polyolefins to increase sharply. These materials are used in small appliance housings, electrical parts and similar applications where they compete with nylon, polyphenylene oxide, polysulfone, and polycarbonate. Accordingly, as the price gap narrows, more of these higher-priced, high-performance materials will be used. Sustained high antimony prices could drive flame retarding ABS, PP, and PE off the market, but substitute materials are available to replace them.

Nylon, polycarbonates, and polysulfones do not generally require additional flame retarders because they are self-extinguishing. Polyphenylene oxide products are often compounded with antimony oxide for additional flame retardance.

Unsaturated polyesters, the resins used extensively in glass-reinforced boats, building products, vehicle bodies, ductwork, etc., consume substantial quantities of flame retarders, but only a small portion is

antimony oxide. Halogenated reactive flame retarders are used extensively, and normally small amounts of antimony flame retarders are used with them to improve overall performance. For example, addition of antimony trioxide permits use of significantly less halogen, which can improve resin viscosity and product weather resistance. Equivalent flame retardance is achieved with these combinations,¹³ which illustrate the "trade-off" between antimony and a halogen in polyester resins.

<u>Bromine</u> <u>Wt. %</u>	<u>Antimony Trioxide</u> <u>Wt. %</u>
17	0
12	1
9	2

In polyester resins, as in PVC, antimony oxide can be replaced by other flame retarders during periods of high prices and short supply. However, some usage will persist where a balance of performance and cost are acceptable. Present consumption of all flame retarders in polyesters is estimated at about 20,000,000 pounds per year. Various industry sources estimate this will increase 2 to 12 times this amount within five years. As much as 5 percent of this will be antimony oxide if prices do not go much above \$1.00 per pound; therefore, unsaturated polyesters are expected to consume substantial amounts of antimony oxide in future years.

c. Rubber Products. Antimony oxide is used with halogens in flame-retarding military rubber goods (mattresses, protective clothing, deck mats, padding, etc.), conveyor belts, hose, cable and various industrial rubber products, particularly for use in hazardous locations, such as mines. Legislation will increase consumption in these product categories as well as in carpet backing, automobile parts, civilian bedding, and others. Antimony oxide appears necessary for these uses and will probably be used at prices up to about \$2.00 per pound.

Consumption reported by the Bureau of Mines is believed to be somewhat conservative. Barring any new national emergency, the outlook is for consumption to increase by about 5 percent annually.

d. Adhesives and Sealants. Substantially more antimony oxide is used in adhesives than is reported to the Bureau of Mines. Flame-retarding adhesives are used to laminate other materials (as in vinyl tarpaulins, vinyl panel facings, and laminated building paper), on special tapes (carpet, aircraft, and electrical), and to bond various assemblies together. Flame-retarding sealants are used in automotive and construction applications. Total 1969 consumption in these categories is estimated at about 2,000,000 pounds of antimony oxide. Phosphorous and halogen compounds should be able to replace antimony oxide in some applications but, in many cases, antimony will continue to be used at prices well over \$1.00 per pound. A construction boom could substantially increase the demand for antimony, but consumption is conservatively estimated to be increasing by about 5 percent annually.

e. Paper. Some high-performance paper building products contain antimony to permit them to conform to building codes, Factory Mutual, or Underwriters Laboratories standards. This use should persist at fairly high antimony prices, since substitutes with the effectiveness and permanence of antimony oxide do not appear to be available. Growth of consumption depends on building and construction activity. This use falls into the "flameproofing chemicals" category of the Bureau of Mines' statistics.

f. Summary of Flame Retarder Uses. The pattern of consumption derived from industry sources differs from that obtained from the Bureau of Mines. An industry-derived pattern of consumption for 1969, along with a projection of consumption to 1975 follows:

Estimated 1969 Consumption			Projected 1975 Consumption*	
Product	Antimony Content	Antimony Trioxide	Antimony Content	Antimony Trioxide
	(Short Tons)	(Lbs)	(Short Tons)	(Lbs)
Plastics	-	9,500,000	-	19,200,000
Adhesives	-	2,000,000	-	2,600,000
Rubber	-	1,100,000	-	1,470,000
Flame-proofing, other	-	<u>3,400,000</u>	-	<u>4,250,000</u>
Total	6,680	16,000,000	11,500	27,520,000

*Based on the assumption that growth will not be hampered by antimony trioxide prices and will result from the following annual product use growth rates: plastics, 12 percent; adhesives, rubber, and others, 5 percent.

Plastics consume about 60 percent of the antimony flame retarders directly. The "flame-proofing, other" category includes: paper, paint, and textiles where antimony oxide is often used with a resin or latex. Accordingly, much of this material is also consumed in plastics systems. Therefore, the future use of antimony trioxide as a flame retarder depends heavily on the economics of its use in plastics and the impact of legislation on use of flame-retarding plastics.

D. Chemical Uses (Other than Flame Retarders)

1. Ceramics. About 3,500,000 pounds of antimony oxide, and 1,100,000 pounds of sodium antimonate (also known as leuconine) are used for ceramic coatings, where the antimony compounds opacify, add hardness, and increase acid resistance. Either compound can be used, but there are enough differences in properties and production techniques that a company usually prefers to use all of one or all of the other for a given period of time. In early 1970, sodium antimonate was selling for \$0.92 per pound (compared to \$1.0750 per

pound for antimony oxide), but approximately 1.3 pounds of sodium antimonate must be used when substituted for one pound of antimony oxide.

In either of the two above forms, antimony is used primarily in dry process enamels on cast iron fixtures for bathrooms and kitchens, such as sinks, bathtubs, and commodes, often called "sanitary ware." There are only five major producers of these items, with plants scattered in seven different states. A typical process consists of adding the antimony compound to the melt batch, and then quenching this in water to get rough granules called frit. The frit is then ground to a powder, colors added, and then further ball-milled. The antimony comprises from 5 percent to 10 percent of the final coating, which is baked onto the plumbing fixture at 1500° to 2000°F. The antimony is probably converted to the pentavalent form.

Tin oxide is actually a better opacifier than antimony and was the primary opacifier many years ago. However, tin oxide has increased in price (to \$2.05 a pound). Then, a zircon product, which had about 65 percent zirconium oxide and 35 percent silicon dioxide, became very popular and cost about \$0.05 per pound. The use of zircon was discontinued in the mid-60's when only A. R. (Acid Resistant) enamels were desired. As much as 10 percent to 18 percent by weight of zircon was needed to get the desired opacity.

Titanium dioxide (at about \$0.24 per pound) is used in some compositions today at a level of 6 percent to 15 percent of the enamel. This oxide has a low coefficient of expansion but often requires oxidants, such as sodium or potassium nitrate, to counteract reducing conditions in smelting. Titanium has better covering power than antimony; therefore, a thinner coat can be used on the substrate.

In addition to the large usage of antimony by the five major plumbing manufacturers mentioned above, other companies use smaller amounts

of antimony and other opacifiers in the production of frits. These frits are used in coating sheet steel. The antimony improves adhesion, gives better leveling, and minimizes "fish eyes" or pinholes.

As a brief summary of advantages and disadvantages, antimony increases hardness and acid resistance, permits a wider range of compositions, and gives a smooth surface. It has less opacity but does not mask the color as much as some other opacifiers. It can cause undesirable color effects, such as a yellow in contact with lead and a white in contact with arsenic. Considering the advantages of these properties, probably antimony will continue to be used in large quantities in ceramics, even if antimony oxide sells for over \$2.00 per pound. At the current level of housing construction in the United States, there will be essentially no growth in the use of antimony in ceramics. However, the rate of housing construction should increase in the near future, and antimony usage in this area should grow about 5 percent per year.

2. Glass. An estimated 1,200,000 pounds per year of antimony oxide and 900,000 pounds of sodium antimonate are used in the glass industry, primarily as a "fining agent." A fining agent helps to produce a uniform melt and good properties in the resultant glass sheet or formed article; air bubbles are minimized, and a very clear, uniform glass product is obtained.

Antimony also acts as a decolorant, and as a desolarant (to prevent darkening with age) in articles such as TV face plates, outdoor glass, and fluorescent lights. Arsenic trioxide (at about \$0.10 per pound) can also be used as a decolorant, but it darkens on exposure to ultraviolet and other wave lengths of light. Antimony can also stabilize certain colors of glass, such as emerald green, without using an oxidizing agent, which is needed with some other additives. The amounts needed can be minimized by the use of a premium grade of silica sand with a low concentration of iron impurities. At the current

antimony oxide price of \$1.075 per pound, this usage should decrease. Replacements could include manganese dioxide, tin oxide, titanium dioxide, arsenic trioxide, barite, cryolite, and fluorspar.

3. Catalysts

a. Antimony Oxide. Approximately $2\frac{1}{2}$ million pounds of antimony oxide are used annually as catalysts in the production of such items as acrylonitrile monomer, polyester fibers, and certain petroleum products.

The production of acrylonitrile monomer is a patented process, with a number of licensees here and abroad. Antimony oxide is used in combination with depleted uranium. This process uses propylene and ammonia as starting raw materials and should continue to grow rapidly while it displaces an earlier catalyst based upon bismuth, phosphorous, and molybdenum.

The use of antimony oxide as a catalyst in the production of polyesters for fibers is also patented; several thousand pounds of polyester can be produced per pound of antimony consumed. Its concentration in the reaction mixture is in the range of 0.025 to 0.075 percent. Compounds of zinc and titanium, which are soluble in glycol, can also be used as catalysts to produce polyesters.

Antimony can be valuable as a catalyst in some petroleum processes to promote certain reactions.

Catalytic uses of antimony oxide should grow at perhaps 25 percent per year for the next two years, then slow down to 10 percent per year. Various other catalysts can be used, particularly those in Group 5 of the periodic table. However, antimony can be used at the predicted rate even at an antimony oxide price over \$2.00 per pound.

b. Antimony Chlorides. Antimony chlorides are used as catalysts in the production of fluorocarbons, such as R-22 and R-13, which are then used as refrigerants, blowing agents, aerosols, textile treatments, etc. About 700,000 pounds of antimony trichloride and antimony pentachloride are used in this manner. The trichloride--also known as antimony butter--is now priced at \$2.60 per pound, compared to \$0.62 at the start of 1969.

4. Stabilizers. About 600,000 pounds of antimony oxide are used annually for the production of colors. In colors, such as yellow and orange, the antimony oxide is an additive that stabilizes the color for use in the paint, printing ink, and plastics industries. In some other pigments, the antimony is actually part of the color, not just an additive. Since the antimony oxide performs so well in preventing fading over a long period of time, this use is expected to grow possibly 10 percent per year, even if antimony prices increase to \$2.00 per pound.

5. Textile Dye Fixative. For many years, potassium antimony tartrate, also known as tartar emetic or tartrated antimony, has been used along with tannic acid in an after-treatment of dyed cloth to improve wash fastness. About two thirds of the 300,000 pounds used per year have been imported.

At today's antimony prices, the use is declining because there are hundreds of liquid fixatives on the market that do acceptable jobs at a lower cost.

A small amount of an NF-grade is used for pharmaceuticals. The tartar emetic could be considered competitive if antimony oxide is not priced above \$1.50 per pound, and if the tartaric acid does not exceed the current price of \$0.43 per pound. In the past year, the price of technical tartar emetic has risen from \$0.84 per pound to over \$2.00.

6. Ammunition, Matches, Fireworks, and Model Rocket Engines.

In the past, significant quantities of antimony sulfide have been used for all of the above purposes. It is still used in ammunition primers, where evidently no substitute has been found. Today, black iron oxide or manganese dioxide has been used in place of antimony sulfide as the striking surface for safety matches. In times of crisis, the small amounts used for specific coloring in fireworks and for model rocket engines could easily be discontinued. Approximately 300,000 pounds of antimony sulfide are used for these four purposes annually.

7. Vulcanization of Rubber. Both antimony oxide and antimony pentasulfide have been used to vulcanize rubber. They improve the heat resistance of the finished product, such as high temperature hose. The service life of boiler hose has been extended as much as ten times over products made with other vulcanizing agents. The annual usage in this application is perhaps only 30,000 pounds. If antimony were to become completely unavailable or extremely high-priced, any polysulfide could be used to do the vulcanization, although in some forms the sulfur is so available that "scorch" results. The alternative would merely mean that the finished article would have to be replaced more frequently.

8. Pigment. At one time, considerable amounts of antimony oxide (and to a lesser extent, antimony sulfide) were used in paint, plastics, and rubber articles as a pigment. Essentially none is used today for its pigment effect. The very large quantities that are used in these industries today are reported under flame retarders.

9. Textile Delusterants. Some synthetic fibers have an undesirable sheen, which can be eliminated by an after-treatment that includes antimony oxide. Although this could be an important small use that might tolerate a very high price

for the oxide, the amount used is probably reported in either the flame retarding or catalyst categories. Titanium dioxide and low-priced calcium carbonate and amorphous silicate are used in much larger volume.

10. Miscellaneous. The following compounds have been made in small amounts at various times, and for a variety of purposes.

- a. Aluminum antimonide
- b. Antimony fluoborate
- c. Antimony isopropylate
- d. Antimony lactate (a. k. a. antimonine)
- e. Antimony pentafluoride
- f. Antimony pentoxide (a. k. a. antimonie acid or antimonie anhydride)
- g. Antimony sulfate
- h. Antimony tartrate
- i. Antimony tetraoxide
- j. Antimony tribromide
- k. Antimony trifluoride
- l. Antimony triiodide
- m. Silver antimony telluride
- n. Zinc antimonide
- o. Antimony tellurate
- p. Potassium pyro antimonate

11. Summary - Chemicals. A summary of antimony chemical uses is given in Table 2.

TABLE 2. Summary - Chemical Use of Antimony

End Use	Chemical Formula	1969		1975 Forecast* Lbs, Sb	Possible Replacement
		Compound	Usage, Lbs Sb		
Ceramics	Sb_2O_3		3,500,000	5,000,000	Tin oxide, titanium dioxide zircon
	$NaSb(OH)_6$		1,100,000		
Glass	Sb_2O_3		1,200,000	1,300,000	Tin oxide, titanium dioxide, arsenic trioxide, barite, fluorspar, manganese dioxide
	$NaSb(OH)_6$		900,000		
Catalyst Antimony Oxide Acrylonitrile Polyesters Miscellaneous	Sb_2O_3		2,500,000	4,200,000	Bismuth phospho-molybdate Various metal organics Numerous
		
		
		
		
Antimony Chlorides	$SbCl_3$	700,000	330,000	500,000	
	$SbCl_5$				
Color Stabilizer	Sb_2O_3		600,000	800,000	Other metallic oxides
	$KSbC_4H_4O_7 \cdot \frac{1}{2}H_2O$		300,000		
Dye Fixative	Sb_2S_3		300,000	200,000	Numerous
		
Ammunition, matches, etc.	Sb_2S_3		300,000	200,000	Numerous
		
Miscellaneous	Many		100,000	250,000	Numerous
		
TOTALS			8,600,000	12,400,000	

*at current antimony oxide prices of \$1.07/lb.

E. Summary of Antimony Consumption and Demand to 1975

1. Consumption. A summary of primary antimony consumption in 1969 and projected demand in 1975 is given in Table 1. Annual growth rates of demand for all end-uses also appear in Table 1 and illustrate the relatively fast or slow growth usage areas.

Disregarding miscellaneous chemicals usage growth, the fastest growing areas of primary antimony demand are as a flame retarder in plastics (12.4 percent) and as a catalyst (11.6 percent). Total flame retarder growth (9.5 percent), colors (8.2 percent), and dye fixative growth (7.0 percent) exceed the annual growth rate projected for total antimony demand (5.8 percent).

All metallurgical uses, other than batteries at a 3 percent annual growth rate, indicate steady or declining demand. Total metallurgical usage is expected to grow at a nominal 1.5 percent per year rate.

The changing pattern of primary antimony usage is illustrated in the following table, which shows the relative demand by major use category in 1969 and 1975:

<u>Application</u>	<u>Percent of Primary Antimony Demand</u>	
	<u>1969</u>	<u>1975</u>
Metallurgical	42	32
Flame Retarders	35	44
Chemicals	<u>23</u>	<u>24</u>
TOTAL	<u>100</u>	<u>100</u>

The projected growth thrust will be in flame retarder applications; chemical uses will maintain their share of demand while the proportions of demand for metallurgical applications, including batteries, will decrease.

TABLE 1 Primary Antimony Consumption in 1969 and Projected Demand to 1975, Tons Metal

Use	1969 Estimated Consumption	1975 Projected Demand	Annual Growth Rate % 1969-1975
<u>Metallurgical</u>			
Batteries	5,950	7,080	3.0
Bearings	750	400	-11.0
Type Metal	400	400	0.0
Solder	225	225	0.0
Cable Covering	150	150	0.0
Ordnance	150	100	-7.0
Other	<u>225</u>	<u>225</u>	<u>0.0</u>
Subtotal	7,850	8,580	1.5
<u>Flame Retardants</u>			
Plastics	3,970	8,000	12.4
Adhesives	830	1,100	4.8
Rubber	460	620	5.1
Other	<u>1,420</u>	<u>1,780</u>	<u>3.8</u>
Subtotal	6,680	11,500	9.5
<u>Chemicals</u>			
Ceramics	1,850	2,500	5.1
Glass	780	650	-3.1
Catalysts	1,215	2,350	11.6
Colors	250	400	8.2
Dye Fixative	50	75	7.0
Pyrophorics	105	100	-0.8
Miscellany	<u>50</u>	<u>125</u>	<u>16.5</u>
Subtotal	<u>4,300</u>	<u>6,200</u>	6.3
Grand Total	<u>18,830</u>	<u>26,280</u>	5.8

2. Supply-Demand Balance. The demand for primary antimony, in the opinion of the NMAB Panel, will increase at a rate of 5.8 percent per year over the 1969-1975 period. This is a very strong demand for one of the less common metals and represents a need in 1975 for some 7,450 short tons of primary metal over the 1969 demand level. Cumulatively, over the 1969-1975 period, an additional 25,000 tons of primary antimony (over 1969 production levels) should be made available to meet projected demands.

From a world production standpoint, production must expand some 1.5 percent annually just to meet U.S. needs. With Japan's needs increasing at a higher rate than the United States and with European needs increasing at a rate close to that of the United States, world demand probably will closely parallel U.S. demand. World production would have to expand to an annual level in excess of 90,000 tons by 1975.

Domestically, where the additional primary metal will be obtained remains the salient question. The U.S. antimony-consuming industry must look to three sources that are listed in order of their importance: domestic, South African, and Bolivian. From published reports on the domestic producing industry's expansion plans, and from knowledge of domestic resources and their economic exploitation, a sharp increase in domestic antimony production seems likely, particularly from Idaho and possibly from Montana. Production from these sources could conceivably reach the level of 2,000 to 3,000 tons per year in the next few years and could provide some 20 to 25 percent of added domestic needs. The actual total potential of these sources could provide the total additional domestic needs, but probably, production expansion would be swift enough and also future antimony prices would not be sufficiently attractive to stimulate rapid expansion.

Barring political interference, Bolivia can and might expand production to satisfy a sizable portion of increased world demand. The resources and production capabilities of Bolivian producers have been proven in the past

(over 14,000 tons per year produced in the 1940's) and, optimistically, this expansion is a possibility.

According to the announced plans of its major antimony producer, South Africa could itself provide all the additional U.S. needs, if political and marketing factors were amenable. Expansion to the announced 30,000 tons per year level from the 1968 production level of about 19,000 tons would alleviate much of the world and domestic demand in the future.

Mexico, as well as the Sino-Soviet Bloc countries, cannot be counted on to supply the expanded needs of the domestic antimony consuming industry.

Although the growth in demand for antimony is reasonably strong as projected at 5.8 percent per year, apparently, domestic sources, as well as African and Bolivian sources, could be stimulated to meet these demands. Any shortages in the metal in the near future should be short term and cyclical; the total supply picture looks reasonable to meet domestic and world needs over the next five years, barring political or conflict (war) factors.

Thus, the future for antimony looks bright as manifested in new demands in flame retarders and chemicals and adequate supplies from domestic or well-known sources. Overall, the supply-demand balance may be temporarily precarious but in reasonable accord over the next five years.

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APPENDIX A

STOCKPILE ACTIVITIES

CONTENTS
(Appendix A)

	<u>Page</u>
I. STOCKPILE OBJECTIVES AND STATUS	61
II. NATIONAL STOCKPILE PURCHASE SPECIFICATIONS	61
A. Antimony Metal	61
B. Antimony Sulphide Ore - Chemical Grade	63
III. ADEQUACY OF STOCKPILE SPECIFICATIONS	64

I. STOCKPILE OBJECTIVES AND STATUS

The stockpile inventory of antimony was 52,985 short tons on June 31, 1964. At that time, the objective was 25,500 short tons.

The General Services Administration received authorization from the Office of Emergency Preparedness (OEP) to dispose of 5,000 short tons of antimony metal or metal equivalent in ore. This authorization was subsequently passed by the Congress under PL-88-615 and signed into law on October 2, 1964. The last sale was made in February 1969.

On July 30, 1969, the stockpile objective was raised to 50,500 short tons but was again revised to 40,700 short tons on April 8, 1970.

A bill is now before the Congress to dispose of 6,000 short tons of antimony metal which is in excess of the objectives. All except 159 tons of this excess is stockpile grade.

Table 12 summarizes the inventory of Government-stockpiled antimony in March 1970.

II. NATIONAL STOCKPILE PURCHASE SPECIFICATIONS (P-2A-R2--March 19, 1962--Supersedes issue of March 7, 1958)

A. Antimony Metal

1. Description. This specification covers refined antimony metal in ingot form, made from ore or other material by processes of reduction and refining, suitable for conversion to antimony oxide and for the production of commercial blends of antimonial lead and battery metal.

2. Chemical and Physical Requirements. Each lot of antimony metal purchased under this specification shall conform to the following applicable chemical and physical requirements:

TABLE 12. Inventory of Government Stockpiled Antimony
March 1970

Chemical Requirements Government Purchase Specifications for Antimony Metal (Grades A and B) Antimony Sulfide Ore, Chemical Grade and Chemical Requirements for Acceptance of Grades C and D Metal into the Stockpile								
Grade of Metal	Form	Pounds	PERCENT BY WEIGHT					
			Antimony Minimum (Sb)	Arsenic Maximum (As)	Sulfur Maximum (S)	Lead Maximum (Pb)		
			Other Elements Each Iron (Fe), Copper (Cu), Nickel (Ni), Tin (Sn), Silver (Ag)					
A	Ingots	15,596,734	99.80	0.05	0.10	0.15	0.001	0.05
A	Slabs	37,387	99.80	0.05	0.10	0.15	0.001	0.05
B	Ingots	56,617,219	99.50	0.10	0.10	0.20	0.001	0.10
B	Slabs	3,350,795	99.50	0.10	0.10	0.20	0.001	0.10
B	Sweepings	10,535	99.50	0.10	0.10	0.20	0.001	0.10
B	Discs	10,421	99.50	0.10	0.10	0.20	0.001	0.10
C	Ingots	2,384,975	99.00	0.30	NA 2/	NA	NA	NA
C	Pigs	654,169	99.00	0.30	NA	NA	NA	NA
C	Broken							
	Pieces	4,279	99.00	0.30	NA	NA	NA	NA
C	Chips	325,541	99.00	0.30	NA	NA	NA	NA
C	Cakes	6,866,843	99.00	0.30	NA	NA	NA	NA
D	Pigs	2,718,357	97.6	2.25	NA	NA	NA	NA
D	Granules	544,683	97.6	2.25	NA	NA	NA	NA
D	Slabs	30,890	97.6	2.25	NA	NA	NA	NA
D	Sweepings	1,202	97.6	2.25	NA	NA	NA	NA
Antimony Sulfide 1/ Ore Chemical Grade		4,340,960	60.00	0.50 max (incl Pb)	Combined S Min. - 22.00	0.50 max (incl As)		
Total Pounds		93,494,990						

1. Total inventory of sulfide ore amounts to 7,875,794 pounds averaging 66.41 percent antimony. Conversion losses to metal were figured at 17 percent. Therefore, the 4,340,960 pounds is the antimony metal equivalent in the ore.

2. Not available.

a. Chemical Requirements

		<u>Percent by Weight</u>	
		<u>Grade A</u>	<u>Grade B</u>
Antimony (Sb)	Min.	99.80	99.50
Arsenic (As)	Max.	0.05	0.10
Sulfur (S)	Max.	0.10	0.10
Lead (Pb)	Max.	0.15	0.20
Selenium (Se)	Max.	0.001	0.001
Other Elements, Each	Max.	0.05	0.10
Iron (Fe), Copper (Cu), Tin (Sn), Silver (Ag), Nickel (Ni)			

b. Physical Requirements. All antimony shall be in ingot form. Ingots shall be of any shape usual with the producer but shall be a minimum of three inches in any dimension and all ingots comprising any lot shall be of the same nominal size and shape. Ingots shall have a clean surface free from dirt, slag, or foreign material.

B. Antimony Sulphide Ore - Chemical Grade

1. Description. This specification covers chemical grade antimony sulphide ore suitable for the production of antimony oxide.

2. Chemical and Physical Requirements

a. Chemical Requirements

Antimony (Sb)	Min.	60.00%
Lead (Pb)	} Combined	Max. 0.50%
Arsenic (As)		
Combined Sulfur (S)	Min.	22.00%

b. Physical Requirements. Ore shall be in its natural state and shall be lumpy and flaky. Not more than 10 percent by weight shall pass a 1/8-inch screen.

3. Packaging. Material may be supplied in bags or any other standard container adequate to protect the material in transit.

III. ADEQUACY OF STOCKPILE SPECIFICATIONS

The specifications for both antimony metal and antimony ore appear to be adequate.

It is recommended that all stockpile material be of as high a quality as possible, so that it can be quickly available for the intended uses in time of national emergency.

In regard to the sulfide ore and concentrates, some producers of antimony oxide prefer to use a finely ground material. However, the "lumpy" material can be ground quite easily if this is necessary. The sulfide type of ore is usually preferred for making high purity antimony oxide.

At the present time, approximately 95 percent of the antimony in the stockpile is in the metal form, and only 5 percent is in ore. The relative amounts of ore and metal in the stockpile should be in the approximate ratio at which these would be required in time of emergency.

Significant amounts of oxide would be needed in an emergency. Most domestic oxide production capacity uses ore rather than metal as the preferred raw material. On this basis, perhaps a higher percentage of stockpile material should be in the form of ore, and a decreased amount in metal.

APPENDIX B

REVIEW OF TECHNICAL LITERATURE

PREFACE

The technical literature review was performed by Dr. Bruce Gonser, consultant, Battelle Columbus Laboratories, under the sponsorship and authority of Mr. Mario Mercado, president, Empresa Minera Unificada S. A. (EMUSA), La Paz, Bolivia. The chairman and members of the NMAB ad hoc Panel on Antimony gratefully acknowledge the assistance of Mr. Mercado and Battelle Columbus Laboratories in making this information available to the industry.

CONTENTS
(Appendix B)

	<u>Page</u>
I. ANTIMONY TECHNICAL LITERATURE REVIEW	71
A. Bibliographies on Antimony	71
B. Books and Encyclopedias	71
C. Annual Reviews	72
D. Technical Articles on Antimony	72
II. AREAS OF ANTIMONY UTILIZATION	73
A. Antimony in Flameproofing Materials	73
1. Fabrics	73
2. Plastics	75
3. Paints and Other Materials	76
B. Sodium Antimonate and Antimony Oxide for Other Than in Flameproofing	78
1. Antimony in Glass	78
2. Vitreous Enamels and Frits	80
3. Antimony Oxide in Paints and Lacquers	81
4. Miscellaneous Oxide Applications	82
C. Antimony Sulfide	82
D. Organic Compounds in Lubricants	83
E. Miscellaneous Compounds of Antimony	84
F. Pure Antimony and Antimony Coatings	84
G. Intermetallic Compounds	87
H. Lead- and Tin-base Alloys	89
1. Battery Plates	89
2. Antimonial Lead, General	90
3. Cable Sheathing	90
4. Lead-Tin-Antimony Alloys	91
5. Tin-Base Alloys	92
6. Pewter and Costume Jewelry	93
7. Antimony in Tin for Low Temperature Use	94

CONTENTS (Continued)
(Appendix B)

	<u>Page</u>
I. <u>Miscellaneous Alloys Containing Antimony</u>	<u>94</u>
1. <u>Brasses and Bronzes</u>	<u>94</u>
2. <u>Aluminum Alloys</u>	<u>95</u>
3. <u>Antimony in Iron and Steel</u>	<u>96</u>
4. <u>Miscellaneous Nonferrous Alloys</u>	<u>97</u>
J. <u>Miscellaneous Items</u>	<u>97</u>
III. <u>REFERENCES</u>	<u>99</u>

I. ANTIMONY TECHNICAL LITERATURE REVIEW

In making this review no attempt has been made to pursue every item pertaining to antimony. The plan has been first to go over the subjects listed in various literature indices to note trends on general fields in which work has been done on antimony. Then, as items were noted that appeared to be pertinent to antimony utilization, selections were made for more detailed abstracting and evaluation. Most of the information reviewed in this report was obtained through listings in the Applied Science and Technology Index, Bibliographies of the Office of Technical Services, U.S. Bureau of Mines publications, and personal literature files. Because of existing bibliographies and literature evaluations on antimony, this review extended only from 1944 to the present.

A. Bibliographies on Antimony

Rather complete coverage of the literature on antimony up to and including 1943 was made a part of previous investigations at Battelle.^{1, 2, 3, 4} Bibliographies of 1932 to 1943 are readily available, including special abstract reviews of literature on: (1) antimony oxide, (2) antimony sulfide in camouflage paint, and (3) analysis of antimony oxide for use in flameproofing fabrics. A bibliography of U.S. Government publications on antimony from 1950 to 1960 is also available.⁵

B. Books and Encyclopedias

Antimony does not enjoy the attention of a metal of construction nor that of some of the newer, more exotic metals. Most of its properties are well known. As a consequence it is considered to be a minor metal and receives rather short space in books and in comprehensive treatments of the elements and their compounds. Wang's book on antimony is still a recognized basic reference.⁶ The 1953 AIME book on Modern Uses of Nonferrous Metals has never been brought up to date but is still a useful compilation of well-established applications.⁷

There are a number of current encyclopediae that carry good discussions on antimony and its compounds, of which the Kirk-Othmer Encyclopedia of Chemical Technology and the Encyclopedia Britannica are among the most complete.^{8, 9, 10, 11, 12} A few books carry single chapters or brief discussions of antimony, but these are usually rather repetitious or superficial regarding applications, unless dealing with a specific subject, such as lead batteries, antimony oxide in ceramics, etc.^{12, 13, 14, 15, 16}

C. Annual Reviews

The best annual reviews of antimony have been those by the U. S. Bureau of Mines. Sections on antimony, which cover uses and technology, are published in both the annual Minerals Yearbook and in Mineral Facts and Problems which is published at five-year intervals.^{17, 18} Unfortunately, such detailed treatment is omitted in the 1966 edition. A valuable part of these reviews has been their list of references. Annual reviews by the Engineering and Mining Journal stress statistics and production, with minor attention to application.¹⁹

Although not giving an annual review, the American Metal Market at times publishes a special section on specific metals which covers various fields of applications. Such a special section on antimony was published in August 1969.^{19b}

D. Technical Articles on Antimony

The various indexes list literally thousands of references to antimony over the last 25 years. Most of these refer to work in chemistry which has involved antimony compounds, or to basic research, where it is difficult to foresee the immediate importance of any findings. Those which bear upon future utilization of antimony, even vaguely, can be discussed best under separate areas of use.

II. AREAS OF ANTIMONY UTILIZATION

A. Antimony in Flameproofing Materials

Since the last survey was made on "Antimony Oxide as a Flameproofing Agent," November 12, 1952,²⁰ frequent references have been made in the technical literature on the increasing importance of flameproofing various materials, on the continued use of antimony oxide, on the growth of a number of other competing, flameproofing agents, and on the increasing importance of flameproofing plastics. One of the best sources of information in this general field is a pamphlet on "Uses of Antimony Compounds as Fire and Flame Retardants." This, complete with bibliography, is published by the Metal and Thermit Division of American Can Co., (M&T Chemicals Inc.).

1. Fabrics. Flameproofing of fabrics, although dating back to the 19th century, was primarily a development for the military services and was applied particularly to canvas duck, at least insofar as antimony is concerned. Following the considerable activity in this field during World War II, the use of antimony trioxide in conjunction with chlorinated organic compounds, such as a chlorinated paraffin or polyvinyl chloride (to yield HCl and generate antimony chloride when decomposed by heat), was applied to a much greater range of fabrics. This at least partially compensated for the loss of much of the wartime market. At the same time research was stimulated on the development of other flame-retardant agents and procedures. Legislation increasingly demanded greater use of flame retardants as a safety measure, particularly in the synthetic fiber field. Standard methods of testing were developed.

One of the more complete references covering this area of development is Little's book on Flameproofing Textile Fabrics.²¹ This comprehensive treatment particularly covers the results of experience and of investigations

through the wartime period. Likewise, a treatise by Ward²² with some 40 references covers well the English technology of flameproofing with antimony oxide up to 1955. This was followed a few years later by a paper by Read and Heighway-Bury²³ that deals specifically with the function of antimony compounds in flameproofing textiles. Among competitive flame retardants developed for cotton in the mid 1950's were various silicon compounds and dibromopropyl phosphates.²⁴ Although antimony trioxide with a chlorinated paraffin has been the most common additive for flameproofing, other forms of antimony have been suggested and used to some extent. As an example, fabric to be flameproofed can be impregnated with sodium carbonate solution, dried, then treated with a 15 percent solution of antimony trichloride in an organic solvent.²⁵

The U. S. Department of Agriculture in recent years has reportedly done some research for the Defense Department to develop more useful fire retardants.²⁶ Antimony oxide has been found not only to be fire-retardant (when used with a chlorinated paraffin) but to filter out fiber-destroying ultraviolet radiation.

A new method for "fireproofing" textiles has been reported recently by the Defense Research Laboratory (materials) in Kanpur, India, which consists of treating the fabric with a 30 percent solution of sodium hexametaphosphate, followed by baking at 170-175°C for eight minutes, then soaking in an 18 percent SbCl_3 solution in methyl alcohol. The dried fabric is soaked in water, excess acid removed by rinsing and treatment with a 5 percent sodium carbonate solution, and finally the fabric is treated with a 4 percent chlorinated rubber solution.²⁷

The use of antimony in this field seems well established, particularly for fabrics used in military applications, but it is by no means without competition. Since antimony oxide has relatively high opacity, it is handicapped

in usage for large areas having a deep color, and it has a delustering effect on some fabrics. Some stiffening of the fabric is associated with the use of antimony in flameproofing, but this varies with the type of weave and is not always undesirable. There is no toxicity problem from the use of antimony compounds. Thus, the antimony oxide - chlorinated compounds process has some limitations in breadth of applications to fabrics, but is easy to apply, withstands dry cleaning and laundering well, and has been a relatively low-cost operation. Aside from some competing materials already mentioned, trimethylolmelamine is used in flameproofing cotton fabric,²⁸ and the Michigan Chemical Corp. has been advertising bromine-base compounds as one of the flame-retardant textile industries' best-known products for application to drapes, carpets and other household fabrics.²⁹ Many of the durable flame-retardant finishes for cotton are based on phosphorous-bearing resins.^{30 a} A rather comprehensive listing of major suppliers of flame-retardant chemicals with type of compound and fabric treated has been published.^{30 b}

2. Plastics^{31, 32, 33} The use of antimony oxide in plastics for flame retardation is a rather recent development, having occurred since any of the previous surveys. This development of flame retardance has been called the key to new plastics markets.³¹

Total use of flame retardants in plastics has been rising at a high rate. The 1968 consumption rate was 12 percent over that for 1967, and indications are that this growth will accelerate even more. General awareness of flammability problems with plastic products, safety legislation, new government standards and new industry codes, as well as the greatly increased volume in the use of plastics, all favor more need for flame-retardant chemicals.

Chlorinated paraffins are used with antimony oxide in this application. The boron compounds are considered to be the most direct replacement for antimony oxide, and their use is expected to grow. Zinc borate can

replace 30 to 70 percent of the antimony oxide in some formulations and, generally, has improved flame-retardant properties such as suppression of afterglow.³²

In addition to flame-retardant chemicals, research may develop new plastics that are inherently flame-retardant. An indication of this is the development and marketing by the Polymer Products Operation, General Electric Co., Selkirk, New York, of a modified phenylene oxide, called NORYL SE-100.³³ From a comparison of prices and properties of competitive materials, it seems that this product should receive considerable attention. However, no comparison is made with an antimony oxide containing product. This is mentioned merely to indicate that this is a highly competitive and rapidly changing field where the future position of no additive is definitely assured. One of the interesting applications of antimony oxide in flameproofing is for reinforced plastics, as polyesters with fiberglass, in panels for the building industry.^{18a} Bromotrichloromethane, which was used at one time in flame-resistant polymers,²⁸ is no longer listed among the additives.

3. Paints and Other Materials. Although fabrics (particularly cotton) and plastics are the most important classes of material in which antimony compounds are used for fireproofing, present and potential applications extend to a wider range. Wood products, paper and other cellulosic materials are amenable to this treatment, but actual usage has been very limited. There are many competing materials and the need has not been as great as for fabrics and plastics. Fordyce³⁴ has described basic components for flameproofing formulations for textiles, paper and wood which include antimony oxide with chlorinated paraffin. Many of the general formulations used in flameproofing apply in general to this wider range of materials. The important field of coated fabrics, which covers combinations of plastics and fabrics, is a large user of the flameproofing products, including antimony oxide.

Another area that deserves mention is in production of paints that are fire resisting. An article in 1964 stresses the British use of antimony oxide in flame-retardant paints, but also mentions impregnating pulpboard with materials that will form antimony chloride on strongly heating.³⁵ The author bewails the fact that so little attention has been given to this property of antimony oxide in books on paints. Although polyvinyl chloride is much used as a chlorinated compound along with antimony trioxide in flameproofing textiles,³⁶ the usual chlorine donors in paints are either plasticizers, such as trichloroethyl phosphate or various chlorinated paraffins. Also, film formers, such as chlorinated waxes or alkyds based on chlorinated dibasic acids, may be used. Usually the proportion is from equal to three times as much chlorinated paraffin as Sb_2O_3 . However, even for flameproofing the antimony oxide content may be only 5 to 10 percent of the total. Titania and other oxides and carbonates form most of the pigment. In the British Isles the Associated Lead Manufacturers market flame-retardant paints containing antimony oxide.

With paints, even more than with plastics and fabrics, antimony oxide has met with severe competition for flameproofing. Where it can be used with advantage because of its contribution to corrosion resistance and in marine applications, the added attribute of fire retardance adds to its desirability.³⁷ A number of articles dealing with fire-resistant paints do not even mention antimony oxide. Considerable emphasis has been given to incorporating compounds which will release HBr on exposure to fire, such as tetrabromo phthalic anhydride in self extinguishing alkyd resins (produced by Michigan Chemical Co.). Also, use of zinc borate or boric acid has received attention in paints that produce insulating foams when strongly heated. Dow Chemical Company has announced a line of fire-retardant phosphorous compounds for use in paints.³⁸ A recent review³⁹ of fire-retardant paints describes various compounds that have been mentioned, but nothing on antimony compounds. This indicates little importance for this application at present.

Considerable investigative work on fire-resistant paints has been done during the past ten years by Harvey Miller and others at the Corps of Engineers Laboratory at Fort Belvoir, Virginia, and also by the U.S. Department of Agriculture, Southern Regional Laboratory, New Orleans, Louisiana. At both places the aim was to test and develop fire-resistant paints for both military and civilian use. The basic formulation at Fort Belvoir has some 13 constituents, including zinc borate, chlorinated paraffin, mono-ammonium phosphate and an alkyd, but no antimony compounds were included in the list of materials. At least some of the results were reported in a series of joint authorship articles.⁴⁰ Silicones have been mentioned as among fire-retardant agents for paints.⁴¹ Although there may be sound reasons for no longer using antimony compounds in fire-resistant paints, further investigation through consultation with manufacturers and the governmental agencies mentioned would seem to be needed to evaluate the situation.

B. Sodium Antimonate and Antimony Oxide for Other Than in Flame-proofing

In this classification are well-known ceramic, glass, vitreous enamel, and paint applications of antimony. Generally, technological advancements in recent years in this area have tended toward substitution or improvements in alternate materials, rather than enhancing the use of antimony. Some of these well-known applications continue to a modest degree, but the situation is not strong either on a marketing or technological basis. A source of general information for this field is the Ceramics Information Center, Battelle Memorial Institute.

1. Antimony in Glass. Antimony oxide is not presently considered to be a glass former, or even an intermediate or additive of importance. In fact, it is not even mentioned in some of the recent publications covering glass compositions or in Shand's Engineering Handbook of Glass.⁴² Tooley, in the 1953

edition of his handbook,⁴³ lists antimony oxide as a minor constituent of some glasses. Thus, in plate glass it has been used in concentrations of up to 1 percent to make the glass more readily melted and worked. Its usefulness has been recognized as a reducing agent toward coloring agents, like chromium, to bring down trivalent chromium. High concentrations, along with arsenic trioxide, have been mentioned to make glasses opaque because of the low solubility and ease of crystallization of antimonates that may form. However, in Tooley's 1960 edition, antimony oxide is not listed in tables of typical compositions of commercial glasses, but is shown only as a 1.32 percent constituent in a special high-germanium glass.

There are indications that antimony oxide was intentionally added to glass even before the 7th century B.C. as an opacifier and later as a decolorizer.⁴⁴ Regardless of its long history of use in glass, the actual role of antimony as an intermediate addition has not been well recognized, since it seemingly has been used for various reasons, none of which have been sufficiently strong to withstand completely the competition of other materials. One of the assets of antimony in glass, however, is that it can exist in both the tri- and penta-valent states, which enables it to act both as a reducing agent under some conditions and as a donor of oxygen in others.

Perhaps the best information on the background of antimony in glass and on possible present usage is Baak and Hornyak's 1966 paper and its 35 references.⁴⁵ Present applications are listed as those of "a refining agent,"⁴⁶ a decolorizer,⁴⁷ an opacifier or coloring agent, and for use in precipitation of metals in glass.^{48, 49} In England, Volk⁵⁰ lists two heat resistant glasses containing 0.07 percent and 0.014 percent antimony oxide, respectively. The presence of 0.4 percent Sb_2O_3 is shown in two out of 14 glass compositions for television tubes. Volk gives one composition of fiberglass containing antimony oxide, and Callinan⁵¹ shows four compositions having 0.7 percent to as high as

15 percent antimony oxide in a group of 83 compositions that were successfully spun into fiber. Mention has been made that as much as 1 percent antimony oxide may be added to glass as a refining agent. Also, arsenic and antimony have been considered to be better refining agents when used for the higher-melting glasses, and antimony is better than arsenic as a decolorizer.⁴⁵

2. Vitreous Enamels and Frits. The best sources of information of this area are the publications of the America Ceramic Society covering enamel bibliographies with abstracts and indices.^{52 a, b, c} Unfortunately, the 1968 issue covering the past decade no longer lists antimony in its index, and individual abstracts must be scanned.

A trend away from antimony in enamels has been pronounced since World War II. Typical of investigations since then has been Kerston's "Behavior of Antimony Compounds in Enamels" in which he recommends titania as an opacifier and for durability in place of sodium antimonate.⁵³ Grube⁵⁴ found the presence of antimony oxide to inhibit opacification normally given by titania plus zinc oxide. German substitution of other opacifiers for antimony and tin oxides during wartime has been discussed.⁵⁵ A comparison of properties of antimony versus zirconia-opacified enamels has been made by King.⁵⁶ In comparing the abrasion resistance of both an antimony-opacified acid-resistant frit and a nonacid-resistant frit with titania and zirconia-opacified frits, the titania coatings gave the best results.⁵⁷

A report by Pavlish and O'Bannon covering some of the work at Battelle on antimony oxide in enamels and glass was published in 1952.⁵⁸ This was not listed in the report on previous work at Battelle.¹

The tendency for antimony to leach out of some enamels was found by Belyaev to be increased by raising the fusing temperature of the enamel frit and glaze.⁵⁹

Among various patents, one of interest covers the improved bonding of enamels to steel by using a bonding compound containing antimony oxide.⁶⁰ Another, by Coffeen, covers an opacifier for vitreous enamels that contains from 54 to 83 percent antimony pentoxide by weight.⁶¹ Coffeen also found, in comparing various antimonates as opacifiers, that barium antimonate most closely approaches sodium antimonate in effectiveness for adding opacity and color.⁶²

A 1961 book on "Porcelain Enamels" by Andrews⁶³ gives a comprehensive account of the industry, the raw materials used, procedures, as well as theoretical background. Antimony oxide and sodium antimonate are classed as opacifiers only. The low antimony enamels contain about 2 percent antimony oxide; high antimony enamels run from 8.5 to 12 percent oxide or 7 to 12.6 percent sodium antimonate. However, the author states that "many of their uses have at present been superseded by zircon and more particularly by titanium enamels." No indication is given of uniqueness which would assure maintenance of the small market that remains.

3. Antimony Oxide in Paints and Lacquers. Antimony trioxide of high purity and optimum particle size has been called the whitest of all pigments.⁶⁴ It was much used in antichalking white outdoor paints a few decades ago, but with the introduction of chalk-resistant titania exterior enamels which were cheaper, and in some respects better, this use for antimony oxide declined rapidly. However, its ease of dispersion in practically all kinds of surface coating vehicles and the improvement it shows in flow properties has caused its retention to a very limited extent as one of the pigment components in current use. About 3 or 4 percent antimony oxide is said to be coprecipitated with titania for some pigments. The largest application, of course, is as a fire-resistant additive which has been covered previously.^{65, 66}

A good source of information for this field is the National Paint Varnish and Lacquer Association, Washington, D. C. (Francis Scofield). A statistical handbook, raw materials index, and abstract reviews are published by this organization.

4. Miscellaneous Oxide Applications. Antimony oxide is used in some plastics, such as floor coverings and plastic insulation for wire, but no details are readily available.⁶⁷

A technique of quantitatively tracing industrial smoke was announced in 1958, whereby finely divided antimony oxide is added to the stream of gases issuing from a given stack. Air samples taken from the surrounding territory are radioactivated and any tracer antimony present is identified. From the amount present, calculations can be made of the distribution of the gases.⁶⁸

Antimony trioxide is commonly added as an activator in producing the calcium halophosphate group of phosphors which are among the most important photoluminescent phosphors.⁶⁹

Although printing inks are sometimes included in past lists of applications of antimony, no specific recent literature references to this use have been found. One book merely states that antimony oxide is "infrequently used," and the "the ink maker has little, if any use for antimony white and cadmium pigments."⁷⁰

C. Antimony Sulfide

The sulfide, as well as the oxide, is used in some vitreous enamels. It has been used successfully as an adherence agent in place of oxides of nickel or cobalt.⁷¹ A frit containing 7 percent antimony trioxide and a mill charge with about 2 percent antimony sulfide is an improvement over the usual sulfide-containing one-coat enamel. It has good adherence with little efflorescence.⁷²

Work at Battelle on infrared transmitting glasses showed that a glass made from potassium pyroantimonate and antimony trisulfide had an average infrared transmission of 42 percent in the 2-7 percent Sb_2O_3 range.⁷³ This was followed by a patent issued to Kelley covering the compositions 2 to 20 parts Sb_2O_3 , 75-97 parts Sb_2S_3 , and 1-10 parts K_2O .⁷⁴

Because of its low color value, the use of antimony trisulfide as a paint pigment has been limited to camouflage paints.⁷⁵ In glass the sulfide is added as a coloring agent to give a ruby color.⁷⁶ This is by no means free of competition. The trisulfide is used in fireworks, matches, and in rubber vulcanization. The pentasulfide is used to produce a red variety of rubber.¹⁰¹

There are many publications on organic and inorganic compounds of antimony which pertain to specific properties or chemical behavior. These are not listed, as their pertinence to utilization of antimony is problematical and most are of slight interest except for basic research. Typical is a recent article on Optical Properties of Antimony Sulfides, or one on the Chemistry and Crystallography of Basic Antimony Sulfates.⁷⁷ However, a few publications on various compounds are of considerable interest.

D. Organic Compounds in Lubricants

Two types of antimony compounds, the dialkyl dithiocarbamates and the dialkyl phosphorodithionates, have been found to show extreme pressure and antiwear properties. Both laboratory bench tests and full-scale evaluation tests have shown these compounds to be multifunctional lubricant additives which act as anticuffing agents, oxidation inhibitors, antiwear agents, and corrosion inhibitors in copper-lead bearings. They have been used (Feb. 1967) in a wide range of commercial lubricants, including automotive and industrial crankcase oils, gear oils, and in both petroleum-base and synthetic-base greases.⁷⁸

E. Miscellaneous Compounds of Antimony

Antimony seems to be getting into the adhesives industry. Radioactivity in black plastic electrical tape and in radioactivity warning labels used in the irradiation of some still samples was traced to antimony-124. It was estimated that the tape and labels contained as much as 1 percent antimony.⁷⁹

In some work done by M&T Chemicals Inc. on barium titanate dielectric bodies, additions of various antimonates were generally unsatisfactory. However, addition of magnesium orthoantimonate was found to shift the Curie peak to a lower temperature, i. e., 1 more percent addition lowered the peak about 60°C.⁸⁰

Organic compounds containing antimony have been patented for use in flame-retardant polyester resins.⁸¹ Aliphatic tertiary stibines are strong reducing agents.¹⁰¹

Lead antimonate, known as Naples Yellow, has been mentioned in a book on ink technology⁷⁰ but no evidence could be found that it was still being used.

F. Pure Antimony and Antimony Coatings

Aside from the use of antimony powder for tracer bullets, there are practically no applications of antimony metal by itself as an end product. However, there is need for the pure metal in making intermetallic compounds for the electronics industry and as a basic material for reagent and research applications. The Central Research Laboratories of the American Smelting and Refining Co. issues descriptive folders covering information and properties of its 99.999+ percent antimony bars. The same purity of metal is produced by Bunker Hill, and by companies in England and Japan.^{18c} An even higher purity of 99.9999 percent has been produced and, presumably, is currently available.

Metallic antimony as a coating is uncommon but is produced for special situations as an electrodeposited relatively pure metal as a replacement coating, a diffused coating, or evaporated coating.

Electrodeposition from a trifluoride electrolyte has the oldest history of usage, but a complex citrate bath is at least equally effective. Bregman⁸² discusses the use of both electrolytes and properties of the deposits. Antimony is unusual among common metals in being resistant to hydrofluoric acid in absence of oxidation. Pure single crystals of antimony have stayed bright for at least 14 years, and a bright, reflective metal surface appears to be possible. In fact, dull to brilliant antimony deposits of any desired thickness have been made on copper or steel from complex citrate baths.⁸³ Although electrodeposited antimony is usually considered to be brittle, some degree of ductility has been attained at times. Bloom⁸⁴ claims ductility, as well as good adherence and high salt spray resistance, for a 0.0015 inch coating on many metals from an antimony trifluoride-ammonium fluoride bath. In addition to electrodeposition for corrosion protection and appearance, a thin coating of antimony has been advocated in surface preparation of enamel base stock to avoid the need for a ground coat in vitreous enameling.⁸⁵ There are occasional references to antimony plating in the Russian technical literature.⁸⁶

Antimony coatings by chemical displacement have been mentioned from time to time in the technical literature, but have achieved little importance. Likewise, the surface coloration of metals by treatment with antimony salts, such as the brown coloration of cadmium-plated articles by immersion in a sodium thioantimonate solution, has been more a curiosity than an industrial development. One simple procedure recommended for replacement coating iron or steel is to immerse the articles in a nearly boiling solution of antimony oxide in caustic soda.⁸⁷ A process of possibly greater interest is to use a replacement coating of

antimony to protect the surface of aluminum and its alloys against some types of corrosion, and provide a suitable undercoating for organic finishes. This is done by immersing the aluminum in a saturated sodium, potassium, or calcium chloride solution containing antimony chloride (2-4 pounds to 3 or 4 quarts of solution) at room temperature.⁸⁸

An antimony-enriched surface may be formed on ferrous articles by pack cementation which is similar to the old methods of chromizing, aluminizing, etc., but this has attracted little attention. Japanese investigators packed iron articles in antimony powder with carbon and sodium carbonate and heated for 30-60 minutes at 550°C to form a two-layer coating about 0.02 mm in thickness. The diffused coating was said to have a beautiful silver luster and better cohesion than by electroplating, but to be relatively brittle.⁸⁹

A procedure for coating nonmetallic acid metallic articles with antimony may have interesting commercial possibilities. This is to take advantage of the high vapor pressure of antimony at comparatively low temperatures and moderate vacuum to evaporate the metal onto exposed surfaces. Aluminum is widely used for coating fabrics, paper, plastics, etc., by this means, and antimony has some advantage in not needing the high vacuum and higher temperature requisite for aluminum evaporation. Very thin coatings of evaporated antimony are ductile and have an excellent appearance. Some development work on coating paper with antimony was held up at one time because of the unfounded fear of toxicity of the product. This has not been covered well in the literature; in fact, mention of antimony evaporation has been limited largely to general discussions of metal evaporation. In some basic work on antimony films it was found that antimony evaporated from elemental antimony existed as Sb_4 molecules, whereas that evaporated from SbAu contained Sb_4 , Sb_2 , and Sb. Films evaporated from SbAu showed super conductivity.^{90, 91}

G. Intermetallic Compounds

Intermetallic compounds of antimony, as well as those of other metals, are notoriously brittle and find little use in normal materials of construction. However, the electronics industry has been able to utilize effectively their semiconductor and associated properties. Basic work in this field at Battelle for the Bradley Mining Company in the early 1950's called attention particularly to the potentialities of AlSb, InSb and GaSb.¹ Since then much research has been done in many countries on these and other intermetallic compounds of antimony.⁹ This is still progressing, and more research by far is being done in this area than in any other field of antimony utilization. Unfortunately, it results in little tonnage use of antimony.

Because of the diffusion of references to antimony compounds in both basic and applied research papers, and to the surprisingly large number of papers, it is not feasible to do more than summarize recent progress in general terms. A special literature survey by a specialist in the field is necessary to evaluate the individual literature items.

Aluminum antimonide, which originally received much attention because of its photoelectric properties, is still a research item but is not currently being utilized in devices. It has some rather poor chemical properties, including lack of adequate resistance to corrosion.⁹²

Indium antimonide currently seems to be the most important inter-metallic compound, particularly as used in infrared filters and in photoconductive devices. It is of less importance in the "Hall effect" industry since indium arsenide is used instead because of its greater effectiveness at higher temperatures. However, InSb may be used effectively at cryogenic temperatures, and there is still interest in its potential in the lower-than-room-temperature area.^{93, 94}

Antimony is used in photomultiplier tubes in combination with cesium and oxygen, i. e., Sb-O-Cs. Many such devices are still being sold although competitive replacements have been developed and are being marketed.

Gallium antimonide has received much attention in the past decade or so. Alloys that include GaSb still have potential and are effective if handled properly but they are termed "irascible" or difficult to control.

Antimony is used in one leg of the bismuth-telluride type of thermoelectric couple which currently is the most commonly used in thermoelectric cooling devices. A higher concentration of antimony is used than bismuth in this one leg, hence about a third of the mass of the cooling element is antimony. Nothing has developed yet to replace this market and it has been growing. An important and unexpected source of information on antimony in the thermoelectric field is Selenium and Tellurium Abstracts, since antimony is frequently associated with tellurium in thermoelectric appliances.^{95, 100} The thermoelectric properties of various other antimony compounds are of interest, such as ZnSb, Ag-Sb-Te, Sb₂Sc₃, BiSb, and CuSbS₂.^{96, 100}

Among some electronic applications of antimony, not based upon intermetallic compounds, are specialty low-melting glasses used for sealants of electronic components. Antimony oxide and oxychloride are used as dopants in silicon devices and microcircuits. This is well established and currently used, but the tonnage is insignificant. Some amorphous semiconductors contain antimony as the sulfide. There are future possibilities in using antimony in disordered semiconductors that will permit formation of 4-compound systems that may have some advantages. However much research is in progress in electronics that use antimony in some form, it is to be stressed that although potentially unexpected usages of antimony may develop the actual tons of metal used is likely to be disappointingly small.

H. Lead- and Tin-base Alloys

This is the area where most of the antimony as metal is used. In general, it is an old, well-established area where antimony is used in minor concentrations throughout a wide range of alloys in many applications. Little work has been done in this area in recent years to establish new or improved materials that contain antimony; rather, more research has been directed toward replacements or improved materials that contain less or no antimony. Among the best sources of information in this area are Lead Abstracts,¹⁰¹ and publications and information from the Tin Research Institute.¹⁰²

1. Battery Plates. The use of antimonial lead in battery grids is probably the best known, and certainly the largest, tonnage use of antimony as metal. Because of the huge scrap return, the amount of primary antimony used is not particularly impressive; however, technological progress in recent years has been to get longer battery life, and to get more power with less weight by casting thinner grids and using thinner separators. Greater strength to compensate for thinner grids would seem to require more antimony as a hardener, but for longer life less antimony is desired. Antimony tends to dissolve in the electrolyte and plate onto the cathode where local cells are set up.¹⁰³ Although no completely satisfactory substitute for antimony in battery grids has been found, the percentage has been reduced from around 7 or 8 percent to about 5 percent and even as low as 3-3/4 percent by some manufacturers in this country.

The range of composition of antimony in battery grids has been listed as 4 to 12 percent, with 0.25 to 0.5 percent tin.⁹ A comprehensive treatment and summary of the literature on lead-acid battery grids was given in 1966 by Drotschmann.¹⁰⁴ Antimonial lead has been compared favorably with calcium-lead, a chief competitor in this field. The role of antimony, aside from physical

effects, is to promote formation of alpha lead dioxide whose prismatic character is beneficial to the cell performance.¹⁰⁵ Stress-corrosion in the grids has been covered recently by A. C. Simon.¹⁰⁶ Of the numerous publications dealing with some phase of battery development or with the subject generally, a few have been listed in the references.^{107, 108, 109, 110, 111}

2. Antimonial Lead, General. Aside from battery grids, antimony is used widely as a hardener of lead and to improve corrosion resistance and attain specific desired properties. Up to 6 percent antimony is used in lead sheet for roofing and flashing.¹¹² There is increased use of lead sheet for noise control and vibration deadening, and this may contain a minor amount of antimony for sufficient hardening to permit proper handling.

Where the lead must withstand stresses without being gradually deformed, a 1 percent antimony addition with 0.05 percent copper has been advocated.¹¹³ Plastic deformation has been found to reduce the tensile strength of 2 - 16 percent antimonial lead, and subsequent heat treatment did not recover the original tensile properties.¹¹⁴ There has been considerable interest in aging properties of lead containing antimony,^{115, 116, 117} and the casting fluidity of lead containing up to 30 percent antimony has been investigated also.¹¹⁸ Maximum fluidity was found in alloys between 17 and 19 percent antimony. Addition of 0.15 percent arsenic was found to increase the rate and extent of hardening of 2 to 10 percent antimony-lead alloys.

The antimony content of hard lead sheet and pipe is listed as 2 to 6 percent.⁹

3. Cable Sheathing. Lead for sheathing cable usually contains from a few tenths to 1 percent antimony, although antimony-free hardeners, such as calcium lead, are also used. The tendency has been to reduce the antimony

content. A cable sheathed in lead, hardened with tin and antimony, and weighing 2,700 tons, was recently laid between Sardinia, Corsica and Italy.¹¹⁹ In Germany, alloys containing 0.2 to 0.4 percent antimony and 0.015 to 0.03 percent arsenic were investigated and compared favorably with lead-copper-tellurium alloys as to fatigue strength, creep strength, and structural stability.¹²⁰ In Russia, suitable cable sheathing has been considered to be lead containing 0.4 to 0.8 percent antimony and 0.005 to 0.2 percent tellurium. The addition of 0.01 to 0.2 percent copper was found to improve resistance to vibration.¹²¹ Although much has been written on cables, cable sheathing, and manufacture, there has been little published recently on the antimony content and factors influencing its use.

4. Lead-Tin-Antimony Alloys. Many lead-base alloys contain both tin and antimony; type metals are a common example. These vary from as low as 2.5 percent for some electrotpe metal to 25 percent antimony in some foundry type metal.¹²³ There has been little development work affecting the use of antimony in this area. Although the quantity of metal in use is huge, the used type is promptly remelted and primary metal consumption is only moderate. In foundry type, 1.5 to 2.0 percent copper is added to give greater hardness and wear resistance.

Another important series of alloys in this area are the lead-base babbitt or bearing metals used in sleeve bearing materials for the automotive and other industries. The diversity and conditions of usage of these bearings have been summarized and compositions outlined in the Metals Handbook¹²⁴ and publications of the Society for Automotive Engineers. SAE lead-base babbitts 13, 14, and 15 contain respectively 10 Sb-6Sn, 15Sb-10Sn, and 15Sb-1Sn-1As. ASTM standard alloy 8, in addition to these, contains 15Sb-5Sn.¹³¹ An arsenical lead-antimony, known in the trade as G. Babbitt, contains 12.75 Sb-0.75 Sn-3As. A rather old but still useful survey has been made to cover the various commercially useful lead-tin-antimony alloys.¹²⁵

In addition to the solid-cast sleeve bearings and liners, many bearing surfaces are formed by electrodeposition. An example, a ternary alloy of 82 lead - 11 tin - 7 antimony is deposited from a fluoborate bath to form a coating for commercial aircraft engine bearings. However, because of its good corrosion resistance and solderability such a ternary alloy has been advocated for printed circuit boards, switchgear bearings, transformer and capacitor cans, etc. The plated product has controllable hardness and has been suggested as a replacement for presently used lead-indium or lead-tin lined aircraft bearings.¹²⁶

5. Tin-Base Alloys. The soft solders, which may be considered either tin-base or lead-base, since they range from 30 to 98 percent lead, normally contain antimony merely as a tolerated impurity of up to 0.5 percent. However, a group of lead-tin-antimony solders containing 1 to 2 percent antimony and 20 to 40 percent tin are well recognized and are used commercially. These antimony-containing solders are somewhat stronger than those that are antimony free, but they cannot be used successfully in soldering galvanized iron. Also, a 95 tin - 5 antimony solder is included in recent standards for applications where a high-melting soft solder is needed for electric motors, generators, radiators and oil coolers.^{127, 128, 129, 130} Of even greater commercial importance is the auto body solder of 5 antimony - 2.5 tin - 0.5 arsenic - balance lead, which is currently being used.

Tin-base babbitts or sleeve bearing liners are large users of antimony in many end-use bearing applications. The softest tin-base bearing metal in common use contains about 7 percent antimony and 3 percent copper; the hardest contain 10 percent antimony and 10 percent copper. However, the ASTM specifications for the four most important compositions cover a range of 4 to 8.5 percent antimony.¹³¹ Commonly, babbitt metal is 88 percent tin, 9 percent antimony, and 2 percent copper.¹³² The whole subject of antimony in both tin- and lead-base bearing metals has been covered recently by Forrester.¹³³ In the

United States, lead-base automotive engine bearings are used almost entirely; in the United Kingdom tin-base is preferred. Many competitive materials have been developed in recent years to replace both tin- and lead-base bearing metals, such as aluminum-base alloys, copper-lead alloys, dry bearings, and various plastics or porous metal-polytetrafluorethylene combinations. Familiarity, ease of casting tin-base babbitts, and excellent performance under light and moderate loads still favor continued use of tin-antimony-copper alloy for many applications.¹³⁴

6. Pewter and Costume Jewelry. With the recent greatly increased price for silver the popularity of good modern pewter has been enhanced. This lead-free pewter may vary slightly in composition with different manufacturers but usually is 92 tin, 6 antimony, and 2 copper. A pewter manufacturers' guild has been formed in the United States to stamp a seal of quality on products that meet their standard in composition and physical properties. They specify 90 percent minimum tin, 2-8 percent antimony, and 0.25 to 2.0 percent copper. Also, the ASTM is establishing a standard for pewter. Some old pewter, which is characterized by turning gray or black rather rapidly, contained from 3 to 50 percent lead, 2 to 7 percent antimony, and about 1 percent copper. There have been no particular technical changes in pewter manufacture in the past 20 years. Most literature on pewter is in manufacturer's sales booklets and a few instruction books for craftsmen on forming the metal. The book "Tin and Its Alloys" is probably the best general reference.^{128b}

Much of the good grade costume jewelry is tin-base metal having about the same composition as pewter. Sometimes a little zinc is added for greater whiteness, but at the cost of more oxidation and difficulties in dross formation on melting and casting. A neoprene-base synthetic rubber mold is commonly used for casting intricately shaped jewelry. From 28 to 30 percent antimony-tin has been used in making die-cast gas meter grids and slides.

Many products are made from tin-base or lead-tin-base alloys containing antimony as a hardener because of the ease of casting the low melting alloys. However, only one of the many tin-bismuth-lead fusible alloys contains antimony. This is Cerromatrix, containing 9 percent antimony. Again, the best general reference for this area of antimony usage is "Tin and Its Alloys."^{134b} More specific information is available from the Tin Research Institute.¹⁰²

7. Antimony in Tin for Low Temperature Use. In addition to the well-known utilization of antimony to enhance mechanical properties of tin, its importance in preventing the transformation of white tin to the gray or alpha form at low temperatures has become recognized. Tests run at Battelle Institute for the Tin Research Institute showed that by inoculation, or contact with alpha tin, the pure metal or normal commercial grades would start to disintegrate to the gray form in a matter of hours, or at least in a few days when held at -40°C . However, with the addition of 0.5 percent antimony, no transformation took place at this temperature for over 5 years, the duration of the test. Codeposition of 0.2 percent antimony in electrodepositing tin has been advocated to assure absence of disintegration for tin-coated products held at low temperatures.¹³⁵ In previous work, tin alloys containing up to 3 percent antimony remained ductile down to -100°C , but with 10 percent antimony, the alloy became brittle below -60°C .¹³¹

I. Miscellaneous Alloys Containing Antimony

1. Brasses and Bronzes. Antimony is not a normal constituent of copper and zinc alloys. Specifications usually limit its use as an impurity, although bronze castings can tolerate a relatively high percentage.¹³⁷ During World War II when there was considerable interest in replacing tin in gear bronzes, a nickel-antimony bronze (90Cu, 8Sb, 2Ni) was developed and used to a limited extent, as indicated in our report of November 25, 1968.¹ Antimony was advocated for use with lead and copper in a bearing alloy also.¹³⁸ Such a

nickel-antimony bronze was claimed to have better wear qualities, equal yield strength, and lower ductility than the normal tin-bearing bronzes. Since then work has been done on improving antimonial bronze alloys for bearings at the U.S. Naval Engineering Experiment Station.¹³⁹ Russian investigators have advocated the use of casting bronzes containing 3 to 7 percent antimony as a base (with copper) and alloyed with one or more additions of phosphorous, lead, nickel, and zinc. This is claimed to have good mechanical and very good anti-friction characteristics and to be a fully satisfactory substitute for tin bronzes in critical components where friction is involved.¹² A recent report on the effect of antimony on the properties of copper base alloys is available.¹⁴⁰

Although normally considered to be undesirable in wrought copper-base alloys, from 0.02 percent to 0.10 percent antimony may be added to prevent dezincification in antimonial naval brass, admiralty metal, and leaded Muntz metal.¹⁴¹ The same amount of arsenic or phosphorous is also effective for the same purpose.¹⁴²

Antimony is a rarity in zinc alloys, but a patent has been noted which claims that addition of 1-5 percent copper, 0.05-0.9 percent antimony, and 0.05-0.9 percent aluminum raises the tensile strength from 17,000 psi to 52,000 psi. The elongation is reduced from 45 to 40 percent.¹⁴³

2. Aluminum Alloys. In attempting to replace tin in cast tin bronzes during World War II, attention was also given to aluminum-base alloys. One group of investigators determined the effects of antimony, zinc, and magnesium. The best alloys found for highly stressed worm gears were aluminum-base containing 2-4 percent antimony, 2 to 7 percent tin, and 2-4 percent magnesium.^{144, 145} These lost strength and hardness at high temperatures, however.

3. Antimony in Iron and Steel. A few items appear from time to time on the effect of antimony on cast iron or other ferrous material.

Addition of antimony was found to lower the strength of cast iron.¹⁴⁶ However, addition of 0.6 percent increased the corrosion resistance against 15 percent sulfuric acid and 10 percent acetic acid by a factor of 1.5 to 2.¹⁴⁷ Klaban¹⁴⁸ found that traces of antimony interfere with crystallization of gray cast iron. Only 0.03-0.06 percent antimony is needed to suppress formation of ferrite. Addition of a trace of antimony gives excellent structural stability at high temperature.

A Soviet review has reported substantially increased hardness and wear resistance of gray cast iron by small additions of antimony.¹⁴⁹ In a study of thermophysical properties, about the only effect of antimony was on thermal conductivity.¹⁵⁰ In investigating lead and antimony in gray iron castings, a Belgian investigator considered antimony to be a detrimental influence, since a 0.12 percent addition provoked formation of an abnormal type of graphite.¹⁵¹

Working the malleable iron, the addition of 0.5 percent antimony was found to increase the microhardness of the ferrite from 125 to 182 kgmm.^{2 152}

In work done by the Cooper Alloy Foundry Company nearly 25 years ago, addition of 0.4-0.6 percent antimony to a stainless steel (27-30 Ni, 10-14 Cr, 3-4 Mo, 3-4 Cu, 0.1 C max, 0.5-0.8 Si, 0.5-0.8 Mn) is claimed to aid in giving excellent resistance to corrosion by hydrochloric, sulfuric, nitric, mixed sulfuric-nitric, mixed hydrofluoric-sulfuric acids, and by calcium hypochlorite. The resistance to attack by hydrochloric acid is attributed to formation of a self-repairing, insoluble antimony film combined with inherent resistance of the alloy. The alloy is recommended for valves, pipe fittings, and castings.¹⁵³

Hot-shortness at the surface of copper-containing mild steel may be caused by antimony or tin since they both reduce the solubility of copper

in austenite. When the solubility is exceeded, a liquid phase is formed in the 1100-1300°C range.¹⁵⁴

Recent studies of magnetic properties of certain iron-antimony alloys indicated that they can have a much larger coercive force than iron alone.¹⁵⁵

4. Miscellaneous Nonferrous Alloys. The possible use of antimony to strengthen alpha-titanium was discussed in a previous report.¹ Later, the Bureau of Mines investigated antimony in titanium and verified the fact that addition of antimony will raise the yield strength without seriously affecting ductility.¹⁵⁶ However, addition of aluminum for a similar purpose is well established, and antimony shows no apparent advantages.

An interesting and logical use for antimony in a minor field has been the codeposition of up to 2 percent with silver from a cyanide electrolyte. The antimony gave 50 percent greater hardness and 10 to 12 times the wear resistance of pure silver. Electrical conductivity was reduced about 50 percent, but this may be important in only a few applications.¹⁵⁷

A silver solder has been patented containing 40 percent silver, 36 percent antimony, and 24 percent copper, with a melting point of around 1,000°F, but no evidence of commercial usage has been noted.¹⁵⁸ No antimony-containing materials have been found in lists of modern, commercially available, hard solders. The silver-antimony system shows a eutectic at 905°F (485°C) with 41 percent antimony, and the copper-antimony system has a eutectic at 979°F (526°C) with 63 percent antimony. Thus, possibilities exist for a low-melting hard solder, but the structure would be such that brittleness would be expected.

J. Miscellaneous Items

Antimony compounds as catalysts have not been well explored, since references are diffusely scattered in chemical literature. An item concerning the catalytic effect of antimony pentoxide in decomposing benzoyl peroxide and some

mixed carbonates was noted.¹⁵⁹ Antimony trichloride and antimony pentachloride are known to be used as catalysts or chlorine carriers in the manufacture of fluorocarbons and carbon tetrachloride.

An important type of commercial photocathode is made by depositing a semitransparent film of antimony on glass (by evaporation) and exposing it to an alkali vapor.^{160, 161}

Antimony in medicines has been reviewed from time to time.¹⁰³ Tartar emetic will cure parasitic infection, protozoal infections, and viral and rickettsial infections. Antimony compounds are at present said to be the choice in treatment of leishmaniasis and schistosomiasis.

In looking for references on antimony use in ammunition, a patent to Imperial Chemical Industries has been noted which claims that antimony compounds, such as tartar emetic (potassium antimony tartrate), when used with colloidal nitrocellulose charges for artillery and small arms, reduces muzzle flash and serves as an antifoulant.¹⁶²

Another patent that is probably too old to be of much importance claims that a conductive coating of metallic antimony applied over a porcelain high-tension insulator prevents radio interference and gives an attractive iridescent surface. Such a coating, by metal spraying, is suggested for road marking.¹⁶³ A later patent suggests incorporating ground metallic antimony into the asphaltic surface of delineated areas, such as traffic lanes. Light is reflected from cleavage planes of the antimony particles.¹⁶⁴

A liquid SO_2 battery using a KCl-SbCl_3 electrolyte was being investigated a few years ago since it was said to offer advantages at sub-zero temperatures.¹⁶⁵

Recently an East German patent was issued to cover the mixing and reaction of antimony and sulfur (in maximum particle size of 10 μ) at a temperature of 100-700°C to give a photoconductor.¹⁶⁶

Antimony in lead as a coating for steel was discussed in a previous report.^{1a} A discussion of the method and procedures used during wartime, including addition of zinc for adherence, has been given by Dr. Bray. The Continental Steel Company in 1944 was commercially using a coating of lead containing 2 percent antimony and 2.5 percent tin to give coatings of 0.4 to 1.1 ounce per square foot.¹⁶⁷

Among the physical properties listed for antimony metal, few are of interest or are outstanding.^{9 to 12, 14, 16} It has rather poor heat and electrical conductivity. The thermoelectric force is unusually high for a metal. One item of unknown origin indicates that 2 to 9 percent antimony in copper gives abnormal expansion at 460-490°C. There are some references in past literature to antimony expanding on freezing. Actually, the pure metal shrinks 0.079 volume percent on solidification.

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Unclassified

Security Classification

1. ORIGINATING ACTIVITY (Concise authority) National Materials Advisory Board Committee on Critical & Strategic Matls. Panel on Antimony		2a. REPORT SECURITY CLASSIFICATION Unclassified	
3. REPORT TITLE TRENDS IN USAGE OF ANTIMONY		2b. GROUP	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report of the Panel on Antimony			
5. AUTHOR(S) (First name, middle initial, last name) NMAB Ad hoc Panel on Antimony			
6. REPORT DATE December 1970		7a. TOTAL NO. OF PAGES 124	7b. NO. OF REFS 180
8a. CONTRACT OR GRANT NO. GS-00-(P)-94008		8b. ORIGINATOR'S REPORT NUMBER(S) NMAB-274	
9. PROJECT NO.		9b. OTHER REPORT NUMBER(S) (Any other numbers that may be assigned this report)	
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
13. ABSTRACT Over the 1969-1975 period, demand for primary antimony is expected to increase at an annual rate of 5.8 percent or to a cumulative additional 25,000 tons of primary antimony over 1969 production levels. Known world resources appear adequate to support present production for the above period. Sustained higher prices may stimulate increased production. Aside from its domestic resources, the U.S. antimony-consuming industry must look to its future sources of material from South Africa, Bolivia, and Australia. As projected to 1975, the fastest growing areas of primary antimony demand are as flame retardants in plastics (12.4% annual growth) and as catalysts (11.6% annual growth). The annual growth rate (5.8%), projected to 1975, for total antimony demand is exceeded by the growth rates of flame retardants (9.5%), colors (8.2%) and dye fixatives (7.0%).			

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6817 National Research Council.
c.1 National Materials Advisory
Board Pub.- NMAB-274

Trends in use of antimony.

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Board Pub.-NMAB-274

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